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A Study of Adhesion in the Cellulose-Starch-Cellulose System

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A STUDY OF ADHESION IN THE CELLULOSE-STARCH-CELLULOSE SYSTEM

A thesis submitted by

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SUMMARY

Adhesion in the system cellulose-water-starch is of great importance to the paper and textile industries, but because of the complexity of the fiber-water system and the lack of direct experimental techniques many gaps exist in the knowledge of this system. This thesis was directed at obtaining a more complete and fundamental understanding of the factors which govern the adhesion of cellulose surfaces as influenced by water, starches, and mechanical parameters.

The complexity of the adhesion system was reduced by developing a method of using films of regenerated cellulose (cellophane) as the adherends rather than fibers. Equipment and procedures were devised for testing of the effective adhesion of the bonds by direct tensile loading of butt joints. Eight amylopectin fractions ranging from 4.8 million to 17,000 molecular weight and four amylose fractions of 1.1 million to 70,000 molecular weight were prepared, characterized by light scattering and viscosity, and generally applied as molecular solutions in order to avoid complications due to the presence of undispersed granules and unknown molecular compositions. The cellophane substrate was characterized by electron microscopy, surface profile measurements, and load-elongation behavior. The mechanical properties of the adhesive fractions were determined on films of the fractions. Bonds were characterized by: their strength, starch content, iodine staining to bring out fracture patterns, evaluation of the extent of diffusion of the adhesive, and by analysis of microtome cross sections.

This research has strong implications for the behavior of high polymer adhesives in the papermaking system. The extreme roughness of fiber surfaces most certainly leads to the observed poor molecular contact within regions of fiber overlap. This study has contributed evidence supporting the view that the use of polymeric beater-adhesives can increase the actual bonded area within fiber bonds by "bridging" the surface discontinuities between fiber surfaces.

Water was only partially effective as an "adhesive" between cellulose adherends because the extent of actual interfacial contact between the cellophane films was low. Effective adhesion of cellophane was increased 60 to 80% by mild abrasion of the surface and an additional 30% by drying under pressure. The nature of the roughening process was critical because adhesion was decreased if large asperities were introduced. The criticalness of adherend contact was confirmed by the fact that a 90° change in the directionality of the extrusion lines on the surfaces of the cellophane caused a 15% change in adhesion, even though the difference in the contours of the two surface directions was only in the order of about 500 A. The effectiveness of water in bonding cellulose surfaces (even as smooth as cellophane) appeared limited by the very low "bridging" capacity of water molecules because of their small size.

Whole fractions of either amylose (1.1×10^6 $\underline{M}_w$ or amylopectin (4.8×10^6 $\underline{M}_w$) proved very effective in establishing molecular "bridges" between the surfaces of the cellulose adherends as evidenced by the fact that the extent of cohesive failure of the adherend surfaces increased from below 5% for the water-cellophane bonds to over 60% for the starch-cellophane bonds. Effective adhesion increased 260%, up to 325 kg./cm.^{2}. There was a very rapid increase in effective adhesion with very small additions of starch and a sharp levelling-off at maximum strength occurred at about 0.15 g./m.^{2} (adhesive thickness, ca. 1000 A.). This experimental value for the minimum amount of adhesive to reach an adhesion maximum agreed closely with calculated values for the void volume between the adherends and with the average height of the "imperfections" of the cellulose surfaces. Based on this it may be concluded that the function of starch adhesives in this system was to "bridge" or fill in the spaces between the two adherend surfaces. Because adhesion was observed to decrease when the amount of adhesive used was greater than the above minimum amount, it was concluded that once total adherend-adhesive-adherend contact

was achieved by filling-in of the voids between the adherends, any additional quantity of adhesive serves merely to separate the adherends and to increase mechanical stress concentration factors which are a strong function of adhesive film thickness.

Amylopectin and amylose both yielded comparable excellent adhesion to cellophane; however, amylopectin always performed well and was not sensitive to experimental conditions as was amylose. Amylose was effective only when its molecular weight was high and when very dilute solutions were used to prepare the bond assemblies. It was found that, as the molecular weight of amylose was reduced, effective adhesion was markedly decreased, even though the cohesive strength and elongation ability of the amylose was not affected. This behavior was shown to be due to an increased rate of retrogradation and higher degree of crystallinity of amylose as its molecular weight was lowered. Since adhesive thickness was controlled with solution concentration, increased retrogradation of amylose as concentration increased also explained why amylose-cellophane adhesion decreased severely when adhesive thickness exceeded about 1000 A.

The weak amylose-cellophane bonds exhibited peel-type failure of the amylose from one of the cellulose surfaces. The above experiments indicated that the adhesion of amylose to cellulose was inhibited by the strong tendency of its molecules to associate in water and, therefore, to be less available for sorption and bonding to the adherends.

Amylopectin was an excellent adhesive for cellulose, regardless of its molecular weight or conditions of its application, provided the molecular weight was above 17,000 (the point where the mechanical properties became poor) and provided that sufficient amylopectin was deposited between the adherends (0.15 g./m.^{2}, 1000 A.). It is apparent that the highly branched structure of amylopectin molecules

kept them from associating in solution and maintained their availability to the adherends during bond assembly preparation.

This insensitivity of adhesion to a molecular weight decrease by a factor of 120 (4.8 million to 39,000) was in contrast to the behavior of amylose. As amylopectin molecular weight was decreased below 5,000,000 to 17,000 up to 70% of the applied amylopectin diffused into the cellophane during bond assembly preparation by evaporation. Correction for the amount of amylopectin "lost" to the bond zone showed that there was no loss in the adhesion effectiveness of the lower molecular weight fractions.

Furthermore, it may be concluded that gross diffusion was not necessary to obtain maximum adhesion because it was found that the amylose and whole amylopectin did not diffuse into the cellophane and still produced the highest level of adhesion. It appeared that if molecular contact between adhesive and adherend was good, no further improvement in adhesion was possible by diffusion.

The mechanical strength and elongation behavior of amylose, amylopectin, and cellophane films was much more meaningful in predicting adhesion behavior when evaluated in the transverse or Z-direction, rather than in the conventional XY direction. It was concluded that the close correspondence of effective adhesion strengths with Z-direction cohesive strengths of the adhesives and adherends was due to the similarity of the testing geometry and specimen size in the two cases. Even though the mechanical properties of amylose were better than amylopectin, the latter was a better adhesive for cellophane because of the better availability of its functional groups during bond formation.

Solvent cleansing of the cellophane resulted in about 20% increase in effective adhesion in the case of cellulose-starch as well as cellulose-water bonds; however, solvent cleansing was not nearly as effective as abrasion (60 to 80%)

in increasing the adhesion in the latter system. The fact that a significant decrease in amylopectin-cellophane adhesion occurred with noncleansed cellophane, even when there was a considerable amount of amylopectin diffusion, indicated that the internal surfaces of the cellophane were also somewhat contaminated. If mechanical interlocking effects were involved significantly, then the observed loss of effective adhesion would not have occurred.

Abrasion of the adherends was found to have a strong negative effect on starch-cellophane adhesion in contrast to the adhesion improvement in the cellophane-water, starch-epoxy, epoxy-cellophane, and the epoxy-metal systems. Stress concentrations appear to have been introduced by abrasion at the starch-cellophane interface because almost total cohesive rupture of the cellophane occurred on bond testing, even though effective adhesion was low. It was concluded that starch molecules (particularly amylopectin) possess such good "gap bridging" ability that sufficiently intimate adhesive-adherend contact is accomplished without abrasion. In contrast, abrasion of the adherend appeared necessary in the other systems mentioned above because of the low "gap bridging" ability of water, the low availability of cellulose molecules in the unabraded cellophane surface, or the low mobility of the viscous epoxy adhesive.

INTRODUCTION

The bonding of cellulose fibers from a water system is considered by many to be the most important and least understood phenomenon occurring in the paper-making process. Various materials of high molecular weight are commonly added to the fiber and water mixture to improve the strength of the resultant paper and to obtain other benefits during the process or in the finished paper. Various starches comprise the largest single class of these additives, which are commonly termed "beater," "wet-end," or headbox adhesives since they are added to the fiber-water mixture prior to formation of the sheet. Estimates of the amount of cornstarch used as a wet-end adhesive range up to about 200,000 tons yearly. Thus, it is very evident that the system cellulose-starch-water is of great importance to the paper industry.

Need exists for a better understanding of cellulose-to-cellulose bonding (adhesion) from the water system, with and without the presence of starch. The fiber, water, and paper systems are complex. There is a serious lack of techniques for directly and independently measuring the strength and extent of fiber-to-fiber bonds as they occur in paper. A further unresolved problem introduced by the use of wet-end adhesives is the determination of the amount, distribution, and nature of the adhesive retained in the paper and in the bonds.

LITERATURE REVIEW

This study involves adhesion of cellulose bonds formed in water-starch systems. The areas of fiber-to-fiber bonding and of starch as a wet-end adhesive are reviewed to demonstrate their close relationship to the present study.

CELLULOSE ADHESION IN THE PAPER SYSTEM

Since almost all of the work on cellulose-to-cellulose adhesion from aqueous systems has been done with fibers, factors involved in their effective bonding are important.

Paper strength is a complex function of (a) the degree, nature, and extent of interfiber bonding, (b) uniformity of sheet structure and bond distribution (formation), (c) individual fiber strength, and (d) fiber structure and dimensions. Wet-end adhesive polymers such as starch probably affect primarily factors (a) and (b).

A consideration of paper structure shows that it is a statistical network which is heterogeneous and anisotropic with respect to the bonding, distribution, and structure of its fiber components. Paper contains a heterogeneous distribution of various-sized voids, gradients of fiber types and sizes through the thickness of the sheet, and a layered structure wherein the fibers lie essentially in non-interweaving planes. The structure and properties of paper have their origins in the fibrillar structure of the cellulose fiber and in fiber interaction with water and other fibers during the forming and drying process. Only the first few percent of water associated with cellulose is firmly bonded; however the "free" water is important in affecting swelling, fiber plasticity, flexibility, collapse, and conformability on drying. The shrinkage of a fiber in its transverse direction is much greater than in its longitudinal direction. This affects the nature of the bonds between fibers and results in imbalanced residual stresses in finished papers.

During the drying process, the fibrous web begins development of hydrogen bonds at between 25 and 45% solid content (1-4). Kallmes and Eckert (5) showed by nitrogen gas adsorption that the areas of fiber known to be optically in contact starting at 45% solids (4) are also close enough together to be hydrogen bonded. From this it is probable that surface tension forces during drying [Campbell (6-8)] are sufficient to bring fiber surfaces which are about 600 A. apart to about 3 A., although recent work (9) has cast doubt on the gas adsorption technique for studies of cellulose surfaces. However, Nissan and Sternstein (10) cite electronmicrographic evidence and give calculations that the actual area of bonding within a fiber contact area is about one-thousandth of the optically "bonded" area. One of the problems in these studies has been a lack of knowledge about the actual three-dimensional structure within the zone of bonding between fibers. The fibrillar elements in a bonded zone may be of varying size distribution and structure and arranged in a limitless number of patterns (11). Page (12) has shown by a direct microscopical technique using polarized light, that very few bonds in paper possess complete optical contact and that bond geometry is indeed complicated. Fiber-to-fiber bond heterogeneity and complexity were illustrated in the classic electron photomicrographs of Asunmaa and Steenberg (13) and Jayme and Hunger (14). The presence of wet-end adhesive polymers probably complicates bond structure and also increases the overall number of bonds in the sheet.

The arrangement of fiber elements, the distribution of the bonded zones, and the structure of the bonds of paper will determine how well it will distribute an externally applied load. Even though stress concentration is widely accepted as a limiting factor in overall paper strength, very little is known about its nature. In all structural materials, nonuniformities introduce internal stress concentrations whenever an external load is applied. This causes initial failure of the material at a lower applied stress than if all elements in the structure shared the load

equally. Paper structure possesses great nonuniformity on the microscopic and molecular scale and, therefore, much stress concentration is possible. Stress distribution in paper has been reviewed by Van den Akker (11, 15-17). Brezinski (18) noted that stress distribution is greatly affected by the number of inter-fiber contacts as altered by wet pressing and beating. Schulz (19) indicated that stressing of paper during drying improves its directional stress-distributing ability by biasing the structural elements of paper in the direction of stress. Leech (20) showed that the use of locust bean gum as a beater adhesive improved the distribution of gross fiber elements in a sheet as measured by Thwing-Albert formation. He found that about 25% of the improvement in paper strength could be attributed to improved paper formation and, thus, to improved stress distribution.

Because of the complexities of paper structure it has been extremely difficult to relate experimental measurements on paper to sheet structure, strength of bonds, and fiber properties. The properties of single fibers have been shown to change markedly (increase in crystallite orientation and elastic modulus) when dried under tension as it occurs in the papermaking process (21). Some progress has been made in using geometric and statistical models theoretically to predict strength, porosity, and optical paper properties from a knowledge of the fiber properties, but much remains unknown.

WET-END ADHESIVES AND STARCH

Since almost all adhesion studies of starch-cellulose which have been reported involve the fiber system, it is important to review the area of wet-end adhesives.

INTRODUCTION

Generally, starch is unmodified for use in the paper furnish; however, modifications such as hypochlorite oxidation, pregelatinization, acetylation, etherification,

and cationization find considerable application. The starch is generally "cooked" at 85 to 95°C. to disrupt the granules prior to its addition to the fibers.

Wet-end adhesives are used to modify the surfaces of cellulosic fibers. Otherwise, this result could be accomplished only by mechanical action at the expense of sheet properties such as opacity, bulk, tearing resistance, etc. Briefly, wet-end adhesives are added for one or a combination of the following (22, 23):

1. Improvement of paper strength;
2. Attainment of comparable paper strength with lower cost raw materials, reduction of power consumption, and/or increase in rate of production;
3. Improvement of sheet uniformity (formation);
4. Production of special papers not otherwise possible with a given furnish or system (e.g., porous or opaque papers of high strength).

Fundamental investigations of the role and mechanism of beater adhesives in fiber-to-fiber bonding are few. Many of the investigations reported are of limited value because one or more of the following factors have not been controlled and/or measured:

1. Quantitative determination of retention in paper.
2. Molecular purity of adhesive.
3. Degree of molecular dispersion of adhesive.
4. Branching and molecular weight of adhesive.
5. Presence (or absence) of fines, foreign ions, and other additives in the sorption system.

GENERAL MECHANISM OF PERFORMANCE OF WET-END ADHESIVES

Interfiber bonding is generally recognized as being the result of the interaction of residual attractive forces which exist on the surfaces of fiber elements. The orientation effect and its special case--hydrogen bonding--are considered of greatest importance in the cellulose-polysaccharide-water beater adhesive system because these materials are highly polar due to their great preponderance of surface hydroxyl groups. The studies of Mann and Marrinan (24-26) on cellulose films using deuterium oxide exchange and infrared absorption spectroscopy indirectly proved the presence of hydrogen bonding in cellulose. Similar techniques were utilized by Corte and Schaschek (27, 28) to indicate hydrogen bonding in paper.

Because the secondary forces of molecular attraction fall off theoretically with the seventh power of distance of separation, fiber elements must be brought within a few Angstrom units to facilitate bond formation by surface tension forces as discussed above. Thus, since solid surfaces generally are very rough and low in mobility on a molecular scale, bringing solids together generally results in relatively little molecular contact for bonding. However, the molecular approach of fiber elements may be facilitated by: (1) increasing the specific surface area of the fibers, (2) increasing the effective flexibility and conformability of the fiber, and (3) the addition of wet-end adhesives. The first two factors are readily achieved by mechanically treating the fibers in the presence of water (beating or refining). For a given degree of mechanical treatment, beater adhesives are thought to increase the number of points of molecular contact between fiber elements which otherwise would be too far separated for bond formation. Leech (20) gave evidence that locust bean gum as a wet-end adhesive contributed to paper strength by increasing bond strength, sheet formation, and bonded area in the proportions of about 60:25:15, respectively. However, it was difficult to assess which and to what extent the following factors caused the increase in bond strength:

1. A greater number of bonds per zone of bonding.

2. Greater individual strength of gum-to-cellulose bonds than cellulose-to-cellulose bonds.

3. More ideal bond structure, i.e., better stress distribution on the bond level.

ADSORPTION AND RETENTION OF STARCH IN PAPER

When native starch granules are heated in water above their gelatinization temperature, the granule structure is disrupted, producing a viscous, colloidal dispersion. However, total dispersion of the molecules does not take place unless high shear action and/or autoclaving under pressure is carried out. The starch molecules tend to be held together in an intermeshing network by secondary forces which correspond to those existing in the ordered regions of the original granules. Furthermore, even if total colloidal disaggregation is achieved, the linear amylose molecules tend to reaggregate into precipitates or gels (retrogradation). It is apparent that many wet-end adhesive studies reported in the literature are meaningless because no distinction was made between (1) colloidally dispersed molecules which sorb onto fiber surfaces prior to sheet formation and (2) molecular aggregates of starch which are mechanically entrapped in the paper during sheet formation. Starch is also retained by coprecipitation and/or electrostatic mechanisms when rosin and alum are used; this further complicates the system.

The studies of Pearl (29) on starch, Most (30) on hemicelluloses, and Russo (31) on locust bean gum indicate the significance of physical sorption in polysaccharide retention. Pearl found that both the linear and the branched molecules of starch (amylose and amylopectin, respectively) were sorbed from aqueous solution by cellulose fibers. Amylose was sorbed more rapidly than amylopectin. Sorption of amylose did not attain equilibrium short of total depletion of the starch in

solution, even after several hundred hours. The initial rates of sorption were rapid (e.g., ca. 0.5% amylose sorbed in the first ten minutes), but decreased quickly with time. The sorption rate was increased by increasing (1) fiber surface area, (2) polymer concentration, and (3) pH, and (4) by decreasing temperature. The sorbed starch fraction was not noticeably desorbed by decreasing its concentration, but was partially removed by increased temperature and pH.

Pearl (29) proposed a retrogradation sorption mechanism to explain his data: amylose was sorbed onto the fiber surfaces followed by sorption of amylose onto the already deposited amylose. Amylose continued depositing on amylose to form a multilayered film of starch on the fibers. It was logical to propose hydrogen bonding between cellulose and amylose as well as between amylose and amylose. In similar fashion, the long external branches of amylopectin molecules were thought to mutually align and form sufficient hydrogen bonds to cause sorption in multilayers.

Pearl's study showed there was no apparent limit to the amount of amylose that cellulose fibers could sorb. This disputed earlier claims of saturation at a 1% level (32-34). Many such confusing claims in starch literature prior to 1942 can be attributed to impure and uncharacterized starch fractions. Also, in contrast to previous beliefs, Pearl was the first to note that amylopectin was sorbed by cellulose.

Cushing (35, 36) and Cushing and Schuman (37) present extensive evidence indicating that the retention of native and chemically modified starches in paper handsheets was dependent on molecular weight, nature of substituent groups, presence or absence of sizing components, order of addition of additives, and the configuration of molecules in solution. They found that retention by bleached sulfite fibers with rosin and alum was severely decreased by increased acid

hydrolysis of the starches (reduction in average molecular weight). Unmodified starches tended toward constant percentage retention with increasing dosage. However, the various thin-boiling (acid-hydrolyzed) starches exhibited decreasing retention as the amount of starch applied was increased. This behavior was attributed to the reduced tendency for molecular association of modified starches. Pretreatment of fibers with guar gum produced increased retention of unmodified starches, but decreased retention of acetylated and etherified starches.

Starch retention by sorption is affected by the type of fiber used. Whether the differences in retention are due to chemical and/or physical variations of the fiber surfaces is not known. Based on rate of sorption of amylose under comparable conditions, Pearl's data (29) indicate the following order of decreasing affinity: cotton linters (slightly beaten), bleached sulfite, alpha, and unbleached kraft. Cushing (36) also found that unbleached kraft fiber retained various starches less effectively than bleached sulfite. In slight disagreement with Pearl, Masirevic and Samec (38) found that 94% alpha pulp had higher sorption capacity than cotton or pulps of both higher and lower alpha content. Pearl (29) also noted that beating of fibers to increase their surface area increased the rate of amylose and amylopectin sorption considerably. Cushing and Schuman (37) found that various chemically substituted as well as native starches were retained better by beaten pulp.

The natural source of starch would be expected to cause great differences in retention in view of the different molecular properties exhibited by different starches. Masirevic and Samec (38) ranked starches in this order of decreasing retention: corn, rice, potato, and wheat. Dittmar and Stein (39), however, ranked them in the order: rice, corn, and potato when alum was employed. Whether these differences were due to inherent variations in starch molecule structure or to differences in the degree of molecular dispersion was not ascertainable from these two studies.

Starch retention in paper by filtration and through precipitation with alum is of no direct import to the present study so this area will not be reviewed. Any study in the area of wet-end adhesives in paper must be cognizant of the importance of the state of molecular dispersion of the starch, for only in those cases where the starch is molecularly dissolved and where alum is absent is it reasonable to assume that the starch is retained only by adsorption onto the fibers.

ADHESION PERFORMANCE OF STARCH IN RELATION TO MOLECULAR ASPECTS

This section reviews those few studies which have considered the effectiveness of adhesion of starch to cellulose as related to molecular properties of starch. Even though the reported studies are essentially indirect and somewhat contradictory since they are applied to complex systems, they will permit the development of hypotheses to be tested in this work.

Effect of Degree of Dispersion

The degree of molecular dispersion of the starch granules upon cooking must be controlled and known; otherwise it is impossible to separate the respective contribution of (1) molecules and (2) granule networks and aggregates. The cooked starch dispersion contains two molecular species--linear amylose and branched amylopectin. Each species is comprised of a broad range of molecular weights. It is reasoned that molecular diffusion brings the molecules close enough to the fiber surfaces so that sufficient segments of any given starch molecule (hydrogen) bond to the fiber surface to be retained. The degree of fit and the number of bonds needed for a starch molecule to be "irreversibly" retained is not known. Basically, a "retained" molecule can do one or more of three things: (1) It may become bonded more extensively to the surface to which it is initially attached or to an adjacent surface on the same fiber. In this case, no gain in interfiber bonding would occur. (2) Segments of a retained molecule may project into a sheet void. This also results

in no gain in bonding. (3) A retained molecule may bond to a fiber element of a different fiber, resulting in a gain in interfiber bonding and, hence, sheet strength and bonded area. It should be emphasized that the percentage of retention remains constant in all three instances. Only the interfiber bonding effectiveness of the retained molecules changes.

Obviously, all retained molecules will not be equally effective because of the probable multilayer structure of the sorbed film. If additional molecules sorb onto already attached starch, they will not be directly helpful in bonding unless they attach to two or more different fiber surfaces. They may, however, act to reinforce starch bridges between fiber elements even though contact with two different surfaces is not accomplished. Cushing and Schuman (37) presented evidence to show that the effectiveness of retained starch molecules changes with time of contact with fibers prior to sheet formation. They reasoned that increased time allowed unattached segments of retained molecules to attach to new surfaces.

The incremental gain in paper strength for a given increment of retained starch decreases as the level of retained starch increases (29). This indicates that the productive association of starch molecules with fiber surfaces (and with each other) decreases as the amount of starch in the sheet increases.

McKenzie (40) found that cationic amylopectin added to unbleached fibers increased in effectiveness with increased molecular dispersion. He reasoned that this was attributable to greater fiber surface covering ability. Pulp with a greater surface area retained more starch and gave less efficiency at a given level of starch in the paper. Paper strength effects caused by adding starch were found to be sensitive to the degree of prior surface area development. Best adhesion results per unit of starch in the paper were obtained with moderately beaten pulps. These results differed from those of Casey (41) who reported that undispersed,

cooked starch granules were more effective than highly dispersed starch when used with lightly beaten pulp, whereas on highly beaten pulp undispersed starch fractions were more effective. This difference may be due to the fact that Casey used rosin and alum. He also found that mechanical dispersion of the swollen starch granules increased burst strength of paper more than molecularly dispersed starch, although the molecular size and branching of the two fractions were undoubtedly different. Conclusions based on Casey's study are difficult because the amounts of the various starches retained were not measured, and the starch fractions were impure and were not characterized.

In a brief study on chemical modification of starches and their effect on peel adhesion from cellulose, McKenzie (42) indicated that acid hydrolysis and oxidation of wheat starch had no effect, whereas carboxymethylation and hydroxyethylation increased adhesion slightly. Amylopectin exhibited better peel adhesion than amylose.

Comparison of Branched and Linear Molecules

Considerable contradiction exists in the literature on whether linear or branched molecules are more effective in increasing adhesion in the cellulose-water system.

Pearl (29) presented what appears to be the most direct study on maize amylose and amylopectin effectiveness. He gave bursting strength data for maize amylose and amylopectin adsorbed onto various pulps without alum or rosin. For amylose sorbed onto bleached sulfite pulp at 400-ml. S.-R. freeness in the range of 0.22 to 4.89% on the weight of the fiber Pearl obtained bursting strength increases of 17 to 55% over the control. For amylopectin on the same pulp he achieved 37 to 52% increases for 0.53 to 1.72% adsorbed. At equivalent amounts of sorption, amylopectin gave about 10 to 30% greater bursting strength values

than did amylose. However, at the lowest level of amylose retention (0.22%) amylose was the most efficient fraction resulting in the greatest increase in strength per unit of starch retained. At the higher levels of sorption, the per unit effectiveness of amylopectin was consistently above that of amylose.

Using laboratory handsheets of bleached kraft of 500-ml. C. S. freeness and rosin and alum, Miller (43) found the application of 2% potato amylopectin increased tensile 10% and burst 19% more than the same dosage of potato amylose. However, in mill trials on bleached sulfite pulp he found waxy maize starch (essentially all amylopectin) to be less effective than a high amylose (65%) maize starch. This was also found by Cushing (35).

McKenzie (42) applied amylose and amylopectin isolated from wheat starch to a bleached kraft pulp which had been made cationic by amine treatment. At 0.5% starch on the fiber he reported that amylopectin increased tensile strength 26% and bursting strength 75% more than did amylose.

Kerr and Shink (44) found that the retention of about 1% of maize amylopectin and waxy maize amylopectin (pregelatinized with borax) gave a 10% and an 18% increase in bursting strength over the control paper using bleached sulfite at 460-ml. C. S. freeness and rosin and alum. However, in contrast to the above studies, no benefit to strength was obtained when 1% amylose was retained.

Masirevic and Samec (38), in contrast to most other workers, found that the addition of different starch fractions to beaten pulps had virtually no effect on paper strength. In sheet impregnation studies, they found no consistent differences between various amyloses and amylopectins. However, they used electrodialysis to obtain the starch fractions, and this method does not yield good separation of the branched and linear fractions.

Jones, et al. (45) found that periodate oxystarches were retained too poorly to be effective as wet-end adhesives. Waxy maize (high-amylopectin) and high-amylose periodate oxidized starch ranked differently depending on whether borax or sodium bisulfite was used to disperse the starch.

Kerr and Shink (46) studied amylose and amylopectin as adhesives in the clay coating of paper. They observed that amylose (applied at 75°C.) was a more effective adhesive than amylopectin (applied at room temperature).

Studies involving molecular properties of nonstarch polysaccharides as they affect bonding between cellulose fibers are also of interest. Thompson, Swanson, and Wise (47) studied hemicellulose and arabogalactans as beater adhesives by sorbing them onto alpha pulp. They found that the magnitude of strength increase due to black spruce hemicellulose was above that expected from starch and below that of guar and locust bean gum. The hexose type of hemicellulose (e.g., coniferous-mannan) produced greater strength gain than the pentose (e.g., deciduous-xylan) type. The addition of 3 to 10% of an arabogalactan extracted from larch with cold water had little or no effect on paper strength. Whether this was a result of high molecular branching or low retention due to high solubility in water was not known.

Swanson (48) and Kärna and Nordman (49) noted that locust bean gum was more effective in increasing paper strength than guar gum. Both polymers are comprised of mannan chains with galactose side groups, but guar gum has a 1:2 ratio of galactose to mannose as compared to a 1:4 ratio for locust bean gum and the degree of branching may be different. Also Gruenhut (50) reported that locust bean gum was sorbed more rapidly than guar. Thus, the difference in effectiveness of these two gums may be due to variations in retention, molecular configuration, or molecular size.

Aaltio and Jouhikainen (51) found that aspen hemicellulose, although very similar in chemical composition to oat xylan, was relatively ineffective in improving strength. They ranked the polysaccharides in the order--locust bean gum, oat xylan, aspen hemicellulose, and sodium alginate when added to a high-alpha, bleached sulfite pulp.

Molecular Weight and Cellulose Adhesion

The effect of molecular size and distribution of starch on adhesion of cellulose has been studied only in limited fashion. Cushing and Schuman (37) added cornstarches hydrolyzed to different degrees to bleached sulfite fibers at high freeness and used rosin and alum. Retention definitely decreased with increasing hydrolysis of the starch; however, there was no correlation between degree of hydrolysis of the starch and paper strength. In fact, several highly degraded fractions, although retained to only one-third of the extent, yielded papers having strength above that resulting from the more highly retained, less degraded starch. Bursting strength was a function of starch hydrolysis and went through a minimum at intermediate hydrolysis. This apparent anomaly may be due to (1) differences in molecule branching or molecular weight distribution, (2) differences in degree of molecular dispersion and/or aggregation of the starch molecules, or (3) two competing mechanisms, e.g., high molecular weight favors cohesion while it restricts molecule diffusion.

McKenzie (42) reported that hydrolysis of wheat starch which was added to cationic fibers resulted in increased paper strength compared to unhydrolyzed at equal levels of starch in the paper. He attributed this to better molecular dispersion of the resultant starch and increased diffusion of the starch molecules into the fibers. Cohesive strength of the films cast from the starch increased and then decreased with hydrolysis. In an earlier study, Houtz (52) found that

the viscosity of various starches dissolved in zinc chloride was generally related to the burst-improving potential of the starch.

Several studies on molecular weight effects of nonstarch polysaccharides should be included. Thompson, Swanson, and Wise (47) found that hydrolysis of isolated spruce hemicelluloses reduced their effectiveness as beater adhesives. They postulated that a critical minimum $\overline{DP}$ (degree of polymerization) of about 40 existed for hemicellulose below which retention and/or adhesiveness became very low. Leech (20) found no significant differences in paper strength as a function of locust bean gum solution viscosity until the viscosity dropped from 117 to 2.2 seconds. Two percent of gum was applied to a bleached sulfite pulp.

Thompson, et al. (47) suggested that the $\overline{DP}$ of wet-end adhesive molecules is important because in cases where a single molecule bridges two cellulose microfibrils together, a minimum $\overline{DP}$ will be needed to span the gap between the fibrils. In addition, if a film or strand is set up between two microfibrils, $\overline{DP}$ will affect the bond through its effect on the cohesive strength of the film. Thus, the theory of the strength of high polymer solids and films as affected by molecular size and size distribution must be considered in the mechanism of cellulose adhesion. This is discussed in the next section.

Cohesive Strength of Starches

Studies on free films of amylose and amylopectins and their acetates generally showed amylose as possessing the greatest film tensile strength, elongation, and flexibility (53-55). Lloyd and Kirst (56) noted that hydrolysis and oxidation of starch fractions increased and then decreased strength of the films, whereas hydroxyethylation and carboxymethylation had little effect. McKenzie (42) noted that in wheat starch hydrolysis, films cast from the starches increased and then decreased in strength with duration of hydrolysis. Wolff, et al. (55) found that corn

amylose starch film strength remained constant until the $\overline{DP}$ was reduced below about 250. Neale (57) in a very early study showed that acid-hydrolyzed or oxidized starches produced films which were weaker than those produced by native starch. Hemstock and Swanson (58) found that oxidized or dextrinized starches yielded weaker clay coatings on paper as the degree of starch degradation increased. Hull and Schoch (59) related the water insolubility of free starch films to the degree of molecular association of the starch. Unmodified cornstarch films were highly associated, while amylopectin films were weakly associated. Starches modified by acid hydrolysis or hydroxyethylation were more soluble than unmodified starches.

Considerable work has been done relating molecular weight, molecular weight distribution, and degree of molecular orientation to the mechanical properties of cellulosic solids (60-64). For cellulose derivatives, a minimum $\overline{DP}$ of 35-85 appears to be needed for mechanical strength. From this level to about 200-400 $\overline{DP}$, mechanical strength increases in rough proportion to $\overline{DP}$. Beyond this $\overline{DP}$ range, the strength then levels off. The presence of molecules below $\overline{DP}$ 400 appears to cause a decrease in strength and elongation properties of films and filaments. The tensile strength of a blend of polymer molecules may be computed by summating the weight fractions and tensile strengths of the individual molecular fractions. Recent work (62-64) showed that the strength of molecular fraction blends does not depend solely on $\overline{DP}_N$ as earlier studies indicated, because breadth of the molecular weight distribution and the degree of molecular orientation also must be considered.

THEORETICAL ASPECTS OF ADHESION (65-84)

INTRODUCTION

Adhesion may be considered as a condition in which two surfaces (the adherends) are joined by an adhesive by means of interfacial forces of molecular attraction

and, in some cases, by mechanical interlocking. In a broader sense, adhesion is a strength attribute of the three-phase system adherend-adhesive-adherend which determines the force or energy needed to separate the adherends. Theoretically, it would be ideal if failure occurred at the exact interface between adhesive and adherend. This is seldom attained in the actual evaluation of real adhesive joints. As discussed by Marra (85) the adhesive phase must act as a stress transfer medium between the two adherends. Because of this, the adhesive must possess adequate cohesive properties. Also, the cohesive and mechanical properties of the adherends themselves are superimposed upon adhesive performance and evaluation.

Adhesion has been practiced for over 3000 years; however, it has been little studied from a scientific viewpoint until the 1950's. Developments have come rather slowly because of the multiplicity of complex interactions which are involved in the adhesion process and because of the great difficulty of controlling and measuring quantitatively these interactions. As was pointed out by Marra (85),

> "There are too many branches of individual sciences involved in adhesion, and very few people exist with sufficient command of all of them to permit the unifying experimentation and rationalization needed to create discipline bridging theories. In addition, adhesion involves the manipulation of material properties not only in bulk, but in colloidal and molecular form, generally involving combinations of several materials or compounds, programmed through critical phase changes---- "

ADHESION BETWEEN SOLIDS WITHOUT AN ADHESIVE

The studies of Bowden and Tabor (86) have shown that metallic and plastic solids which are very smooth and free from absorbed gases and impurities can adhere to one another with strengths approaching those of the cohesive strength of the solids themselves. However, most solids are rough, hard, and contaminated. Consequently, their real area of interfacial contact is only a small fraction of the apparent area. Even the most carefully polished or cleaned surfaces contain surface imperfections

that are large compared with molecular dimensions (72, 86). Specially polished plate glass and mirror-polished steel have surface irregularities ranging from 100 to 300 A. in size. Solid surfaces are held apart by these irregularities and cannot be brought into really close contact over a substantial area. Exceptions to this are carefully cleaved and selected surfaces of mica crystals which are smooth to within several Angstrom units. Such mica surfaces may be put back together to yield almost the same bonding strength as the cohesive strength of mica (87). The presence of organic contaminants, oxides, and water vapor greatly reduces the adhesion between solids (86). Also, there is a loss in adhesion following the release of elastic strains which result when one surface is pressed against another to achieve contact (86).

Thus, a major role of adhesives appears to be that of "bridging-the-gaps" between the adherends in order to achieve a high interfacial contact and facilitate the action of intermolecular forces. Because of the large imperfections present in real solid surfaces large molecules appear necessary to provide the bridging function. It is not surprising that virtually all adhesives are (or become) high polymers. These molecules can attach themselves to both adherends at multiple points, thereby bridging the discontinuities with a continuous, coherent structure.

MOLECULAR FORCES

The forces responsible for molecular adhesion are essentially the same as those responsible for the cohesion of solids, namely primary and secondary valence forces (75, 88-90).

The secondary forces are those generally involved in adhesion. They are of four types: viz. London-dispersion, Keesom-orientation, Debye-induction, and hydrogen bonds. Their interaction energies range up to about 10 kcal. per mole

with hydrogen bonds being the strongest, the orientation forces ranking second, then the dispersion forces, followed by the relatively weak induction forces. The basic nature of these forces is electrical in nature and is due to the fact that most molecules have polarity, i.e., have separated (or separatable) centers of positive and negative charge. The more asymmetric the molecule the greater the dipole moment and the greater the attraction. Orientation forces are interactions between permanent dipoles whereby the positive and negative centers attract each other and also exert an orienting effect on other molecules. Induction forces have their origin in the capacity of nonpolar molecules to become polarized under the influence of other molecules which have strong dipole moments. Dispersion forces are universal forces of great importance to all intermolecular systems, but especially if there are no polar molecules involved. These forces are due to the fact that at any given instant the electron clouds of any given molecule are not symmetrical and, thus the molecule possesses a momentary dipole. These instantaneous dipoles can then interact in the same fashion as the orientation or induction effects and have the advantage of being additive.

Simplified equations for the above three secondary forces have been derived and show an inverse seventh power relationship with distance of separation between the centers of the dipoles. Experimental determinations of the forces between solid surfaces have recently been discussed by Debye (88) where an inverse fourth power dependence of attractive force with distance was obtained. The difference in these two cases is attributable to the relatively large distances between the experimental surfaces and to more complicated interactions between real solids as compared to isolated, independent molecules.

The hydrogen bond is of the greatest importance to the adhesion study at hand because it is strongly involved in the cellulose, water, and starch systems. The hydrogen bond is an especially strong bond and is based on polarity like the above

secondary bonds. The bond is considered basically electrostatic in nature involving resonance hybridization of structures. The single valence electron of the hydrogen atom cannot fully "shield" the positive nucleus and the hydrogen then interacts between two electronegative centers such as oxygen, fluorine, and nitrogen.

The molecular force fields of atoms or molecules on the surface of a solid are not balanced by the surrounding bulk molecules as are those molecules in the bulk of the solid. Therefore, a net free surface energy exists on all surfaces which is the source of attractive energy. This energy explains adsorption, wetting, heats of immersion and adsorption, and, of course, adhesion.

The effects of hydrogen bonding and polar groups on adhesion were revealed by McLaren and coworkers (91-93) in their studies on the adhesion of high polymers to cellulose. They found that peel adhesion was linearly related to carboxyl group content of the adhesive and polar group concentration on the cellulose surface.

The relation between molecular forces and adhesive bond failure is not known beyond a first approximation. Czyzak (94) calculated adhesion values by using dipole and dispersion forces constants and vectorial summation of the forces for simple molecules on metals. He obtained values about 10 times higher than found in experimental adhesion measurements. Taylor and Rutzler (95) fitted atom models of polymers onto plane surfaces representing the atomic dimensions of metals and metal oxides to approximate the "fit" which could be obtained in an adhesive-adherend system. Even after allowing for the exclusion of a high proportion of bonding sites due to distance and steric effects, calculated values based on theoretical forces were at least ten times higher than experimental. It is suggested that failure initially occurs at weak zones that are the result of localized stress accumulations and flaws. Other explanations (67, 71) offered to account for the high calculated results are:

1. Only very few interaction sites can be obtained between the adhesive and the adherend surface.

2. Theoretical interaction energies are too high because of impurities at the interface.

3. The interface is stronger than adjacent layers in the adhesive, and adhesion therefore reflects the strength of the bulk adhesive alone.

4. Thermodynamic calculations are based on ideal reversibility which may not be applicable to an adhesive system. Tangential failure along a surface requires less force than calculated from thermodynamics. Also, considerable energy is consumed in causing flow of the materials in a bond even though this does not create sufficient additional surface.

Likewise, the real cohesive strength of most solid materials is several orders of magnitude smaller than that which may be calculated from the arrangement of atoms and the internal molecular forces between them. This has led to the Griffith theory of flaws (96) as a means of explaining the lower strength. This theory predicts that the critical stress for fracture should vary inversely as the square root of the flaw size and that the critical stress is proportional to the square root of the Young's modulus and the specific surface energy of the solid. Experimental evidence on the effects of flaw size distribution affirms this approach for brittle solids, but where ductile flow occurs as in polymeric solids the analysis becomes very difficult, for the relations of changes in molecules or molecular structure to observed changes in bulk properties and strength have not been satisfactorily explained (97). There remains an inadequate understanding of the failure processes themselves and their dependence on molecular and structural parameters. The rupture process is discontinuous and it has, therefore, been impossible to follow the process theoretically using a continuous set of variables as can be done in studying flow processes in solids.

Mention should be made of studies to calculate the strength of hydrogen-bonded systems such as cellulose and starch. Nissan (99) and Nissan and Sternstein

(10) developed theories for the cellulose system and calculated the strength of a single hydrogen bond as 10^{-5} dynes. Regenerated rayon fibers have a shear strength of about 1800 kg./cm.^{2}, whereas individually measured, cellulose fiber-to-fiber bonds were found to be only 59 kg./cm.^{2} (98). Nissan attributed low interfacial contact area in fiber bonds as the cause for this difference, although comparison of these two systems may be invalid because of the gross differences in bond geometrics and stress concentration factors. Stamm (101) summarizes a group of comparisons of theoretical vs. experimental adhesion and cohesion strengths for hydrogen bonded systems and observes that the theoretical force is 3 to 13 times greater than the experimental. Fowkes (100) using dispersion force calculations showed that the strength of the polyethylene bond to iron should be 11,200 kg./cm.^{2}, but measured tensile strengths are one to two orders of magnitude lower.

It is evident that in the cases of both adhesion and cohesion of solids, calculations of rupture strength based on molecular forces and interatomic distances are low, and that rupture phenomena are based more on local structural features than on mean molecular attractions.

THEORIES AND CONCEPTS OF ADHESION

Adsorption Theory of Adhesion

Most investigators believe that the most fundamental prerequisite for good adhesion is uniform and unlimited molecular contact between the adherends. This view is the basis for the adsorption theory of adhesion. Molecular forces between two materials are theoretically sufficient for strong adhesion; however, real systems do not approach this strength because of imperfect contact. Huntsberger (102) points out that there are three causes for limited interfacial contact:

1. Thermodynamic: equilibrium between the molecules of the adhesive and adherend is not achieved.

2. Thermodynamic equilibrium between the adhesive and adherend does not correspond to maximum interfacial contact.

3. Molecular configuration and/or packing at equilibrium between the two phases is not conducive to a high proportion of interfacial contacts.

Thus, wetting of the solid by the adhesive prior to its solidification to achieve good interfacial molecular contact is acknowledged to be a most critical factor in adhesion. Figure 1 shows the balance of surface energies involved when a liquid drop is at equilibrium on a solid surface.

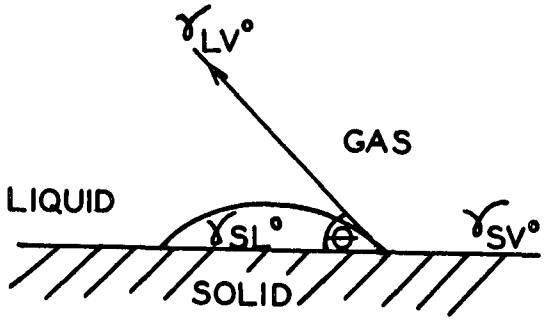

Figure 1. Force Balance of a Liquid Drop on a Solid

The Young and Dupré relation showing the relation of surface tensions and contact angle, θ, is:

$$\gamma_{SV^{\circ}} = \gamma_{SL} + \gamma_{LV^{\circ}} \cos \theta \qquad (1)$$

where γ is the surface tension, the subscripts $\underline{SV^{\circ}}$ and $\underline{LV^{\circ}}$ refer to the solid and liquid in equilibrium with the saturated vapor, respectively, and $\underline{SL}$ to the interfacial tension between the solid and the liquid. Many researchers equate surface tension directly to surface free energy, but care is needed here because this is true only at thermodynamic equilibrium and holds generally only for pure liquids.

If the liquid is removed from the solid, two surfaces are created (solid and liquid-vapor) and one interface (solid-liquid) is destroyed. The net energy change

$(\gamma_{S^o}+\gamma_{LV^o}-\gamma_{SL})$ is referred to as the reversible work of adhesion $\underline{W_A}$:

$$W_A = \gamma_{S^o} + \gamma_{LV^o} - \gamma_{SL} \qquad (2)$$

where γ_{S^o} is the surface tension of the solid in a vacuum. However, because of the strong adsorption forces existing between the solid and the vapor, the experimental value of the work of adhesion, referred to as the equilibrium reversible work of adhesion, $\underline{W_A}'$, is

$$W_A' = \gamma_{SV^o} + \gamma_{LV^o} - \gamma_{SL}. \qquad (3)$$

Substituting γ_{SL} from Equation (1) into (3) yields:

$$W_A' = \gamma_{LV^o} (1 + \cos\theta). \qquad (4)$$

If one were to break the liquid phase cohesively there would be a gain in two surfaces of the liquid but no loss of an interface would occur; therefore the work of "adhesion" (more correctly, the work of cohesion, $\underline{W_c}$) is:

$$W_c = 2\gamma_{LV^o} \qquad (5)$$

Bangham and Rozouk (103) combined Equations (2), (3), and (4) to yield:

$$W_A = \gamma_{LV^o} (1 + \cos\theta) + (\gamma_{S^o} - \gamma_{SV^o}) \qquad (6)$$

where $(\gamma_{S^o} - \gamma_{SV^o})$, the spreading pressure, may be evaluated as the energy change occurring when a solid is immersed in the saturated vapor of the liquid. These workers also proved that this energy change is always positive and, therefore, $\underline{W_A} > \underline{W_A}'$ by the amount $(\gamma_{S^o} - \gamma_{SV^o})$. This means that it requires more work to remove a liquid completely from a solid than to remove the liquid and leave an equilibrium film of adsorbed vapor of the liquid. Also, since the work of cohesion of the liquid is $2\gamma_{LV^o}$, Equation (6) indicates that when $\theta = 0$, the reversible work of adhesion, $\underline{W_A}$, exceeds the work of cohesion $(2\gamma_{LV^o})$, by $(\gamma_{S^o} - \gamma_{SV^o})$.

Bowden and Tabor (86) indicated that where the quantity ($\gamma_{S^o} - \gamma_{SV^o}$) in Equation (6) is significant, the interface must give higher energy for the first layer than for subsequent layers, which makes it unlikely that adhesive failure will occur at the adhesive-adherend interface. Bikerman (72) has also suggested, on a statistical probability basis, that adhesive failure never occurs at an interface provided adequate wetting of the surface is achieved and a weak boundary layer does not exist.

The Young and Dupré Equation (1) describes only the state of wetting at equilibrium and not the criteria for its occurrence. The criteria for a liquid to spread or wet a solid, were developed by Cooper and Nuttall (104) and Harkins (105) where the initial spreading coefficient, S, must be greater than 0 for spreading and

$$S = \gamma_{S^o} - (\gamma_{LV^o} + \gamma_{SL}). \tag{7}$$

From Equations (2), (5), and (7):

$$S = W_A - W_c . \tag{8}$$

Thus, for spreading to take place, the work of adhesion must be greater than the work of cohesion (and, therefore, the contact angle must be close to zero). For materials of similar molecular composition or forces, $\gamma_{SL} \ll \gamma_{LV^o}$; therefore, Equation (7) may be simplified to

$$S = \gamma_{S^o} - \gamma_{LV^o}. \tag{9}$$

Thus, for spreading to occur $\gamma_{S^o} > \gamma_{LV^o}$, i.e., high energy solids and low energy liquids favor spreading of the liquid and the wetting of the solid by the liquid.

Sharpe and Schonhorn (106) combined the spreading coefficient approach with Zisman's technique (107) for obtaining an approximation of the surface free energy

of a solid. Zisman extrapolated the contact angles produced on a solid by a homologous series of liquids. The extrapolated surface tension at $\theta = 0$ was called the critical surface tension of the solid, γ_c. This value was shown to be a good estimate of the free surface energy of the solid only when polar forces were absent. If such is the case, Equation (9) becomes:

$$S = \gamma_c - \gamma_{LV} \tag{10}$$

and spreading may be predicted by substracting the surface tension of the liquid from the critical surface tension of the solid. Sharpe and Schonhorn (106) pointed out that the basic requirement for a strong adhesive bond is that the surface energy of the adhesive be below that of the adherend. In fact, good bonding between polyethylene and epoxy resins was obtained by causing polyethylene to wet epoxy, while the opposite is known to be unsatisfactory. The thermodynamic requirements for spreading are necessary but insufficient criteria for obtaining good bonds. Considerations of rate of wetting, surface geometry, flaws, and stress concentrations must be included.

It should be pointed out that surface roughness and geometry influence contact angles (108, 109). Roughening a surface results in an apparent contact angle with a liquid less than the true contact angle (if the liquid has a true contact angle less than 90°). Furthermore, the more voids a surface has, the higher the apparent contact angle becomes.

The driving force which determines wetting rate, in the absence of external pressure, is capillary pressure, ΔP. Zisman (107) has shown that capillary pressure is a maximum when γ_{LV° has the value

$$\gamma_{LV^\circ} = 1/2(\gamma_c + 1/b) \tag{11}$$

where γ_c is the critical surface tension of the solid and b is a function of

solid-liquid interaction. Since the capillarity equation is

$$\Delta P = \gamma_{LV^o} (1/R_1 + 1/R_2) \tag{12}$$

then

$$P_{max} = 1/2(\gamma_c + 1/b)(1/R_1 + 1/R_2) \tag{13}$$

where R_1 and R_2 are the radii of curvature of the liquid-vapor interfaces in the nonwetted interstices. Equation (13) shows the great importance of surface structure and geometry in achieving optimum interfacial contact. Viscosity and rheology of the liquid, changes in liquid properties with concentration and temperature are factors which affect the capillary pressure and rate of wetting. Capillary structure and surface geometry of the substrate, and changes in the substrate due to swelling, shrinking, or flowing under pressure are also involved.

In connection with the adsorption theory of adhesion, a few studies should be mentioned. DeBruyne (66) was the initial developer of this theory based on the fact that the same adhesive could be used for various adherends and that no chemical reaction was possible due to the inertness of the materials. His polarity rule (polar adhesives will bond only polar adherends and that nonpolar adhesives will bond only nonpolar adherends) has been shown to be incorrect for some systems (106) because a nonpolar adhesive can wet and adhere to a polar surface which normally has a higher surface energy than the adhesive.

McLaren and coworkers (91-93) developed the adsorption theory further with their studies of the adhesion of high polymers to cellulose. They stressed the importance of high temperatures and low viscosities of the adhesive to promote migration and approach to the adherend surface. The second stage, adsorption at the interface, could then occur through the action of secondary valence forces. McLaren found that peel strength of polymer adhesion was proportional to the

concentration of polar groups (carboxyl) on the polymer chains raised to the 0.5 to 0.7 power. The interrelationships of adhesion with dielectric constant, dipole moment, viscosity, and tack temperature of the polymers were also studied. The correlation between polymer polarity and adhesion was not clear cut due to the stresses which developed during solidification of the adhesive. For example, they found that crystallization of a polymer at the interface reduced adhesion. They indicated that hot-melt polymers must have sufficiently low viscosity during solidification to minimize dimensional changes at the interface which would disrupt bonding.

It has proven very difficult to correlate molecular constants such as dipole moment and dielectric constants with adhesion because they cannot be measured on polymers with accuracy and because of the indirectness of rupture testing of adhesion. For example, DeLollis, et al. (110) found no correlation between dielectric constants of the adhesive and substrate vs. adhesion.

A final complicating factor should be emphasized; that of the configuration and nature of adsorbed polymers on a solid. It is generally recognized that in polymer adsorption, only a small fraction of the possible bonding groups on a polymer are attached to the adherend. Also, molecular weight equilibrium is achieved only very slowly and is very probably not achieved in most adhesion studies. Thus, low molecular weight polymer molecules probably will tend to be concentrated on the adherend.

In summary of the adsorption theory of adhesion we may conclude that wetting of the adherend by the adhesive is necessary to achieve high interfacial contact, with the result that the close molecular approach will provide opportunity for intermolecular forces to form. Low contact angles predict good wetting if equilibrium can be achieved. The rate of approach to equilibrium is governed by

capillary pressures which are very dependent on surface geometry. A balance between rate and equilibrium often indicates that the optimum work of adhesion is obtained at finite contact angles (102).

Because real surfaces have complex geometries which cannot be well defined and because high polymer adhesives pass through configurational and phase changes on adsorption and solidification, the thermodynamics discussed above can serve only as guidelines to interpretation and cannot be expected to describe closely real adhesive bonds.

Mechanical Theory of Adhesion

The early researches of McBain (111) resulted in his conclusion of the existence of two types of adhesive bonds: (1) specific or chemical bonds between smooth, dense surfaces and which involve secondary valence forces and (2) mechanical bonds between porous surfaces which involve penetration and hooking or anchoring of the dried adhesive with no need for intermolecular molecular forces. Mechanical adhesion is believed by some (74) to be the key mechanism in the cases of adherends such as paper, cloth, and wood; however, almost all workers feel that even in these porous systems specific adhesion due to molecular forces is of greater importance. Marian and Stumbo (78) state that even a nail in wood is held by friction which has been proven by Bowden and Tabor (86) to be caused by physicochemical forces.

Browne and coworkers (112) described a series of experiments which refuted many of McBain's claims for mechanical adhesion. Bikerman (74) feels that proof for mechanical adhesion lies in the insensitivity of such bonds to impurities which cause weak boundary layers. However, Swanson and Becher (113) showed that the presence of surface impurities had a large negative effect on the adhesion of extruded polyethylene to paper. Adhesion of polyethylene to cellulose was also increased by surface oxidation. This was attributed to the increase in the

surface free energy of the solid. Of course these observations do not necessarily prove that mechanical adhesion is not also involved because it is possible that the increase in the surface energy of the adherend also increases the rate and extent of wetting by the adhesive which results in more penetration into the fine capillaries. This could increase mechanical hooking as well as the strength and area of intermolecular bonding.

It is apparent that it is difficult experimentally to separate the specific and mechanical effects. The most successful attempt was that of Marian and Wissing (114) who treated wood with silanes which reacted with the hydroxyl groups to block them without affecting the structure of the wood. Even though less than a monolayer of silane was present, shear adhesion tests on the wood blocks showed an 80 to 90% loss in adhesion due to the silane treatment. Penetration of the adhesives was the same in both cases. These experiments indicate that specific adhesion through intermolecular forces is of greater importance than mechanical adhesion, even in a system where considerable penetration of adhesive is present. In line with the above conclusion, Suchsland (115) found that when wood possessed a smooth and undamaged surface, penetration of the adhesive was not necessary for adhesion.

Electrical Theory of Adhesion

Skinner and coworkers (116) and Deryaguin and coworkers (117), explained the increase found in the work of stripping a polymer film from an adherend with increase in rate of stripping as being due to electrostatic attraction between charged layers at the interface. Also, they felt that the action of intermolecular forces should be independent of velocity of testing. The adhesion force was compared to that of attraction between oppositely charged plates in a condenser. The electrostatic theory was supported by studying the occurrence of electrical discharge during the breaking of certain joints.

It is probable that the observed electrical effects are indicative of a consequence of adhesion rather than a cause. Voyutskii (80) summarized the limitations of this theory, the key ones being: (1) no charge effects are noted in many systems which adhere well, (2) treatments which do not affect charge potential change adhesion markedly, and (3) adhesion of nonpolar and similar substances is not explained.

Diffusion Theory of Adhesion

The diffusion theory of adhesion of Voyutskii and coworkers (80) states that adhesion is a result of interdiffusion of polymer molecules or of their individual segments across the adhesive-adherend interface so that, upon completion of the bonding process, the interface no longer exists. Thus, adhesion is visualized as an interfacial mutual solubility phenomenon as contrasted to a surface phenomenon, as in the case of the adsorption and electrical theories. Adhesion becomes a volume phenomenon rather than a surface one and adhesive strength becomes that of the cohesive strength of the adhesive-adherend solid "solution." The diffusion theory is thought to explain the dependence of the work of stripping on the rate of stripping, whereas the adsorption theory fails to do so.

Most of the studies have been carried out using elastomeric polymers and have indicated that diffusion (1) is inversely proportional to molecular weight, (2) increases with temperature and time of contact, and (3) is dependent on the molecular compatibility of the adhesive and adherend as judged by solubility parameter and similarity in polarity.

Voyutskii (80) makes no claim for the ultimate source of adhesion other than stating it is a result of either the action of intermolecular forces or mechanical interlocking of the mutually mixed polymer molecules. Thus, from this standpoint the diffusion theory of adhesion is an extension of the specific adhesion or

adsorption theory and the mechanical theory. The mutual penetration of the molecules in the formation of the adhesive bond may be looked upon as simply leading to an increase in the extent of intermolecular contact. Patrikeev (118) calculated that a 5 to 10 A. mutual diffusion of molecules across an interface yields a three-to-fivefold increase in surface area of contact.

Vasenin (119) gave an approximate mathematical treatment of Voyutskii's work and showed that the adhesion between two nonpolar polymers is inversely proportional to the 2/3 power of the molecular weight and directly proportional to the 2/3 power of the number of effective branches on the polymer. Branching of a molecule increases the entropy and therefore favors diffusion, requiring less energy for the process than in the case of linear molecules. Also, a branched molecule is smaller than a linear one of the same molecular weight. The depth of diffusion of a polymer was found to be proportional to the force of adhesion and was believed dependent on the temperature, the nature of the adhesive and substrate, the configuration of the polymer molecules, and time. Voyutskii (80) noted that adhesion between cellophane and a polar copolymer markedly increased with conditioning temperature and with aging times up to 80 days. It was found that increased polarity did not always increase bond strength to a polar adherend as suggested by the McLaren school (91-93). This anomaly was explained by hypothesizing that increased polarity causes greater mutual solubility which favors diffusion and adhesion, but that polymer chain flexibility and mobility are decreased by high polarity causing a reduction in diffusion and adhesion. Thus, the effect of polar groups in adhesion appears to depend upon a balance between these competing phenomena. The ratio of adhesion to molecular weight went through a maximum because lower molecular weight molecules cause low cohesive strength of the adhesive while higher molecular weight molecules diffuse slower (80).

Weidner and Crocker (71) point out that Voyutskii's ideas have some qualitative validity in adhesion between similar polymers; however, they doubted that cellophane had any porosity toward hydrocarbon liquids and elastomeric polymers. They felt that the conclusion that heating increased the mutual solubility of the copolymer and cellophane was unwarranted because solvent coating was used to apply the adhesive. In contrast, they suggested that the heating caused a stress relaxation in the polymer film increasing cohesion. Weidner and Crocker (71) state:

> "A diffusion theory of adhesion...should explain why adhesion of polymers (to cellophane) is lowered to the vanishing point as soon as cellophane is wetted with water. Diffusion of polymer can hardly reverse itself so rapidly..."

They felt that a good portion of diffusion theory experimental results can be explained on the basis of polymer response to an interface, i.e., time, pressure, temperature, and low viscosity all favor interfacial conformance, with temperature able to produce a level of wetting and stress relaxation that neither time nor pressure can usually achieve.

Rheological Theory of Adhesion

Bikerman (72) feels that the strength of an experimental adhesive bond has only a small relation to molecular adhesion, because when such a bond is ruptured, failure practically never proceeds along the adhesive-adherend interface; therefore for a proper bond (not possessing a weak boundary layer) the forces between the adhesive and adherend do not influence the measured force to break the joint. Rupture occurs cohesively within one of the materials and, therefore, is a rheological problem. Bikerman feels that a well-defined interface often does not exist due to interdiffusion and penetration and that if it exists separation along an exactly predetermined, complicated path is statistically improbable. He indicates that most of the work expended in breaking a joint is due to deformation of materials.

Improper joints are described by Bikerman (72) as those which contain weak boundary layers between the adhesive and adherend. Thus, with incomplete wetting (based on the criteria discussed under adsorption theory of adhesion) air may contribute to improper joint formation. Impurities such as low molecular weight solvents, lubricants, antioxidants and other additives may reduce the strength of the adhesive or may adsorb on the adherends to create wetting problems. He feels that the only bond that will fail exactly at an adhesive-adherend interface is an improper one.

Proper joints according to Bikerman (72) are those which are free from boundary layer problems. He summarizes the experimental strength of a proper joint to be:

$$F = 1/\alpha[(C/\beta) - \delta] \qquad (14)$$

where F is the observed experimental strength, α is a stress concentration factor due to differences in the mechanical properties of the adhesive and adherend, β is the stress concentration factor due to the flaws and heterogeneity of the adhesive and adherend, C is the cohesive strength of the adhesive if it breaks rather than the adherend and if deformation is ideally Hookian, and δ is the frozen-in stress created during the solidification process of bond formation. From this equation it is evident that Bikerman equates adhesion to the cohesive strength of the adhesive when stress concentration factors are unity and frozen-in stresses are absent. Bikerman feels the factor β may vary from 10 to 1000 depending on the nature of the adhesive and the solidification process. As an approximation, the ratio (C/β) is the strength of the adhesive. The value α becomes smaller as the difference between the moduli of elasticity of adhesive and adherend decreases. The frozen-in stress, δ, may be reduced by using an adhesive which contracts during solidification to the same extent as the adherend or which can relax stresses during solidification.

In testing butt joints two-to-fiftyfold radial stress concentrations can develop along the three-phase boundary, adhesive-adherend-air, especially for thick adhesive layers (72). Thus, α of Equation (14) may be 2 to 50.

Thin joints normally can withstand greater stressing loads than thick ones. Bikerman attributes this to the fact that all three stress concentration terms α, β, and δ change with thickness. Stress distribution patterns during loading will be dependent on adhesive thickness. The earlier study of Meissner and Baldauf (120) established the stress concentration mechanism of the thickness-strength rule. However, for small values of the ratio of thickness to diameter they found that the amount of adhesive in the bond was so small that its tendency to contract produced negligible stresses near the interface and that the internal stress causing failure was substantially equal to the externally applied stress. They also indicated that internal stresses which develop during cooling or shrinking of the adhesive increase with the thickness of the joint.

SUMMARY OF ADHESION

The adhesion in any system depends on:

1. Actual strength of secondary bonds due to interaction of surface energies.
2. The extent and perfection of contact between adhesive and adherend.
3. Presence or absence of flaws and impurities at the interface or within the adhesive.
4. Presence or absence of other stress concentration effects caused by variations in cross section, dimensional changes during drying or conditioning, and differences in the mechanical and rheological properties of adhesive and adherend.

Many of the researchers have concerned themselves with only certain aspects of the entire system which accounts for the lack of acceptance of any one theory

for adhesion. Furthermore, a good proportion of the disagreement between the various theories is due to semantics.

We must agree that both molecular nearness and a high area of contact between the adhesive and adherend is necessary. Therefore wetting, spreading, and penetration aspects are critical. Most people agree, also, that adsorption of the adhesive molecules on the solid occurs with the establishment of secondary (and, in the case of chemically reactive groups, primary) intermolecular bonds. Certainly thermodynamics, surface energy, heats of adsorption, entropy changes, etc., are concepts which cannot be ignored in connection with wetting, adsorption, and intermolecular bonding. Secondary (and in some systems, primary) bonds are important in determining both the cohesive strength and the mechanical constants of the adhesives and adherends.

Although theories of kinetics and thermodynamics are helpful to establish criteria and boundaries and to explain overall mechanisms for good adhesion, real adhesive joints are also dependent on localized stress concentration flaws and other heterogeneities of solid-to-solid systems which must be considered if adhesive theory and performance are to be comparable. The experimental strength of a bond is the maximum theoretical adhesive strength of the bond less the strength losses caused by (1) nonideal wetting and adsorption, (2) internal stresses, and (3) imperfect stressing during testing. Thus, the measured strength of any particular system is dependent on the nature of the adhesive and adherend, the history and conditions of adhesive application and solidification, the surface and pore structure of the adherend, the physical and flow properties of the components, the design of the bond, and the bond testing technique.

PRESENTATION OF THE PROBLEM

Review of the literature showed that no systematic study exists which explains the role of molecular and other physicochemical properties of starch in affecting the adhesion between cellulose surfaces as they are bonded from a water system. As a step toward a more fundamental understanding of the mechanism of wet-end adhesive performance, it is proposed to examine certain critical factors of the adhesion of cellulose surfaces with water and with starches applied from aqueous solutions.

Because of the complexities of the fiber and paper system and the lack of techniques for measuring directly and independently the strength and extent of fiber-to-fiber bonds as they occur in paper, a technique is needed for localizing the bonded surfaces in order to permit their study. Regenerated cellulose film (cellophane) was selected as the adherend for this study because it offered a simplified bond geometry, is relatively smooth and pure, and possesses a molecular composition very similar to cellulose-fiber. With a few exceptions, all starch fractions used were pure fractions in true solution in order to avoid complications due to the presence of undispersed granules and unknown molecular compositions.

Because cellulose, starch, and water are strongly polar, capable of hydrogen bonding, and so similar in molecular structure, problems should be minimized regarding thermodynamic equilibrium and rate of wetting. The thermodynamic work of adhesion of water-cellulose, water-starch, cellulose-starch, as well as the work of cohesion of cellulose and starch and water are very similar (101). Therefore, it is reasonable to assume that differences observed in the adhesion behavior of cellulose, water, and aqueous starch solutions are attributable to factors other than free surface energy and wetting.

The factors of greatest concern for this study are the molecular characteristics of the branched and linear fractions of starch, i.e., amylopectin and amylose, respectively. The following hypotheses regarding the adhesive behavior of these starch fractions in the water-cellulose system are proposed for testing in this study:

1. The degree of contact between the two cellulose surfaces involved in a bond is a critical factor in achieving high levels of adhesion, regardless of whether the contact is achieved by pressure, water, or the addition of branched or linear fractions of starch.

2. Maximum adhesion is dependent on the molecular size of the adhesive. There exists a critical molecular weight for amylose and amylopectin below which adhesion is reduced in proportion to loss of cohesive strength and deformability of the adhesive.

3. It is believed that since branched and linear fractions of starch exhibit different molecular behavior in water, this should be reflected in adhesive behavior with cellulose. Based on thermodynamics, both should be equally efficacious as adhesives. However, greater availability of hydroxyl groups during bond formation would favor the amylopectin fraction of starch because amylose molecules have a greater tendency to associate with themselves and to present fewer opportunities for cellulose-starch molecular interaction. Thus, the better mechanical properties of amylose films may be counteracted by the fact that the molecules are "less available" than branched for bonding to another solid.

4. The mechanical properties of the adhesive and adherend are closely related to adhesion; however, the most relevant properties are those evaluated using similar testing geometry and specimen size as in the adhesive bonds themselves. Once

maximum surface contact is achieved, any increase in amount of adhesive used should result in decreased adhesion due to mechanical factors.

5. The surface structure of the cellulose adherend should introduce mechanical stress concentration effects which would have a significant effect on adhesion and the nature of bond failure.

6. The amount of adhesive needed to achieve optimum adhesion should correspond to the amount required by the particular adherend to just "bridge" and "fill in" the spaces between the two surfaces of the adhesive joint.

Of particular interest to this study is the relation of cellulose adhesion with certain physicochemical features of starch using water as the experimental control. It is the broad goal of this study to add to the fundamental knowledge of cellulose adhesion in order that wet-end adhesives may be utilized more effectively.

EXPERIMENTAL PROCEDURES, MATERIALS, AND EQUIPMENT

THE OVERALL SYSTEM

The basic system considered in this program was made of two adherends bonded together by a single layer of adhesive. The two adherends were identical in all cases and consisted of specially cleaned, wet regenerated cellulose (cellophane) films. The adhesives were specially prepared starch fractions, and were applied between the cellophane films as dilute aqueous solutions.

The cellophane-starch-cellophane bond assemblies were dried under restraint on plate glass. Specimens for the testing of bond strength were cut out of the film assemblies and bonded between pairs of metal test cylinders using an epoxy adhesive. For testing, each pair of cylinders containing one film-starch-film bond assembly was attached to a special two-part jig mounted in a tensile tester.

CELLOPHANE

Almost all of the studies were carried out using specially cleaned commercial cellophane as the substrate or adherend. The cellophane supplied by the E. I. du Pont de Nemours Company was designated as 193 PUD-0. This film was manufactured from cellulose xanthate without the addition of plasticizers or surface treatments and, therefore, can be considered relatively "pure" cellulose. The films had a thickness of 0.001 $\pm$ 0.0001 inch.

Some of the initial experiments were carried out using never-dried gel cellophane obtained through the courtesy of the Olin Mathieson Chemical Corporation.

HANDLING AND CLEANSING OF CELLOPHANE FILM

The PUD-0 film was subjected to extensive cleaning prior to use; however, a small number of experiments were carried out with cellophane that had been water-soaked and rinsed only.

A study of the effect of surface cleansing of the cellophane was made using the following sequences of reagents:

1. Water only
2. Ethanol, water
3. Carbon tetrachloride, ethanol, water
4. Carbon tetrachloride, ethanol, water, 7-1/2% sodium hydroxide, water
5. Carbon tetrachloride vapor
6. Trichloroethylene vapor

The individual films were flushed six times in the reagents held in pyrex glass trays. Following each reagent bath, both sides of the films were thoroughly sprayed with fresh reagent using a wash bottle. To avoid the contamination of a given bath with reagent from a preceding bath, each sheet was spray-washed with solvent of the same identity as the bath into which the sheet was to be placed. The spray liquids were kept separate from the baths. To clarify the steps used in the standard washing sequence, Table I is presented.

Contamination of the baths and the films was minimized by handling the films with specially designed stainless steel triangular frames equipped with stainless steel spring clips. All glassware and frames were cleaned just prior to use with alcoholic-KOH solution followed by a thorough rinse in distilled water.

Vapor-phase cleaning of the cellophane films was carried out in several cases by hanging two films simultaneously in a large battery jar, placing a small amount of carbon tetrachloride or trichloroethylene in the bottom of the jar, covering the jar with plate glass, and heating the solvent on a hot-plate to cause the solvent to reflux and the vapors to condense on the films.

Following cleansing and prior to use, all films were stored in distilled water for a minimum of two hours. Just before use the films were given a final spray

rinse with distilled water which had been freed of dust by filtration through a membrane filter (pore size, 2500 A.).

TABLE I

STANDARD SEQUENCE FOR WASHING CELLOPHANE

Step	Reagent[a]	Method of Reagent Application
1	Carbon tetrachloride	Bath
2	Carbon tetrachloride	Spray
3	95% Ethanol	Spray
4	95% Ethanol	Bath
5	95% Ethanol	Spray
6	Distilled water	Spray
7	Distilled water	Bath
8	Distilled water	Bath
9	Distilled water[b]	Bath
10	Distilled water[c]	Spray

[a] Carbon tetrachloride and ethanol were reagent grade.
[b] Films stored for at least two hours in last bath prior to use.
[c] Water was first filtered through a 2500 A. membrane filter.

MEASUREMENT OF SURFACE CONFIGURATION OF CELLOPHANE

Determinations of the surface irregularities of both the PUD-0 and gel cellophane were made using a Brush Surface Analyzer (Brush Electronics Company, Cleveland, Ohio). This instrument is based on the principle of electronic amplification and recording of the deflection of a 0.0005-inch stylus as it moved on the surface being measured. With proper calibration, surface imperfections in the order of 100 to 200 A. may be evaluated by this technique.

The cellophane specimens were prepared for analysis by soaking in distilled water for two hours and drying them under restraint against plate glass. The above wetting and drying sequence was done in order to reproduce the conditions to which the cellophane was exposed during bond preparation.

Brush traces were made for both sides of each type of cellophane and in the "with"- and "cross"-machine directions. The traces were evaluated by:

1. Counting the total number of imperfections which exceeded 1480 A. (5.8 microinches), and
2. Averaging the magnitude of pen deflections above and below the reference line (which represented the "plane of the cellophane surface").

Each determination involved an average of 60 deflection values from a 3-cm. trace of cellophane surface.

ELECTRON PHOTOMICROGRAPHY

Electron photomicrographs were taken of replicas of several cellophane surfaces to characterize the surfaces before and after adhesion failure. The specimens were first shadowed with palladium at an angle of 30°. Carbon was vaporized onto the palladium to give more mechanical strength to the palladium film. Cellophane was then dissolved from the replica with sulfuric acid and sodium hydroxide.

The electron microscope was an EMU-3F R.C.A. unit, operated at 50 kilovolts to give magnifications after threefold photographic enlargements ranging from 16,900 to 99,000 diameters.

SURFACE ROUGHENING OF CELLOPHANE

During the course of the experimental work it was found necessary to roughen the surface of the cellophane film so that the test specimens made from them would

adhere sufficiently to the metal cylinders used for bond testing. Therefore, prior to solvent cleansing, one surface of each film was abraded gently but thoroughly with fine emery powder (American Optical Company, No. 303). The abrading operation was carried out manually with a 3 by 5 by 1/4-inch soft felt pad backed with a brass plate. This tool permitted the application of a reproducible, low pressure of 0.12 p.s.i., transmitted through the felt to the cellophane. The films were roughened prior to solvent cleansing.

The cellophane film (usually 8-1/2 by 11-inch) was taped to a glass plate, the emery dust sprinkled on the film, and the felt-brass tool moved manually in rotary fashion with no hand pressure over the emery dust. The cellophane surfaces were abraded until they became uniformly opalescent (400 strokes). The films were gently brushed with a camel's hair brush to remove the free emery dust and then subjected to the standard washing cycle. Inspection of the abraded and cleaned film with a microscope indicated no trace of residual emery grains.

MECHANICAL PROPERTIES OF CELLOPHANE

The mechanical properties of the cellophane used in this study were evaluated in three directions: viz., machine direction, cross-machine direction, and the Z- or transverse-direction (stress perpendicular to plane of film). The cellophane films were soaked in water and dried against plate glass in order to reproduce bond preparation conditions.

The machine- and cross-machine direction properties were determined with an Instron Universal Testing Machine. This instrument was fitted with line-contact clamps which permitted the accurate control of clamping pressure and the testing span length. A constant rate of straining (0.13 cm./min.) was applied to the specimen clamped at an initial span length of 1.27 cm. The stress-strain diagrams

were analyzed to yield ultimate strength, elongation at break, elongation at proportional limit, proportional limit, and elastic modulus.

The transverse-direction strength of cellophane was evaluated under conditions which exactly duplicated those of bond preparation and testing which are described later. The cellophane was cleaned and roughened as described above to attain sufficient adhesion. Individual specimens were adhered directly to steel test cylinders using epoxy adhesive.

STARCH FRACTIONS

All starch fractions used in this study came from two sources. The amylose fractions were prepared from NEPOL, a maize amylose manufactured by the A. E. Staley Manufacturing Company. The amylopectin fractions were prepared from waxy maize starch (AMIOCA pearl) supplied through the courtesy of National Starch and Chemical Corporation.

PURIFICATION OF WHOLE AMYLOSE

The NEPOL is manufactured from cornstarch by a differential precipitation technique. The manufacturer gives its composition as 90% amylose, 1.5% noncarbohydrates, 1.0% cellulosics, and 0.5% ash. Presumably, the remaining 7% consists of amylopectin. Attempts to remove the mineral components in NEPOL by column extraction with water were unsuccessful. Recrystallization with butanol was used for purification (see below).

Extraction of Fatty Substances from Whole Amylose

In order to obviate possible interferences of fatty materials in adhesion and iodine colorimetry, the whole amylose was extracted with 85% (vol./vol.) aqueous methanol. The procedure used was a modification of that suggested by Schoch (121).

A 2000-gram bath of NEPOL was added slowly with mechanical stirring to 7000 ml. of 85% methanol. This mixture was poured into a 12-liter, two-necked flask and boiled under reflux with continuous stirring for 3 hours. While still hot, the mixture was filtered through a Buchner funnel, reslurried in 4 liters of methanol (reagent), filtered again, and then washed successively with three 1-liter portions of methanol. The refluxing and washing procedure was repeated four times. Following the final washes, the starch was air-dried for 24 hours and sealed in glass jars.

LIQUID AMMONIA PRETREATMENT OF WHOLE AMYLOSE

Portions of the extracted amylose were treated with liquid ammonia in an effort to render the material soluble in water at a later time without having to resort to autoclaving. This technique was reported to be highly successful for natural starches and to cause no apparent degradation (122).

Regrettably, various liquid ammonia-treated amyloses were not fully soluble in water, even when heated and stirred for one hour at 95°C. On the basis of several attempts it was concluded that liquid ammonia pretreatment was not efficacious in rendering the amylose of this present study water soluble at atmospheric pressure.

DISPERSION OF AMYLOSE AND PREPARATION OF BUTANOL COMPLEXES

The complexing of amylose with butanol facilitated its storage for the subsequent experimental work. A reactive hot-water soluble amylose was obtained by a modification of the technique developed by Schoch and coworkers (123, 124). Basically, the approach was to: (1) dissolve the dry whole amylose (methanol-extracted) by autoclaving in the presence of butanol and water, (2) cool the solution to permit the formation of crystals of the amylose-butanol complex, and (3) isolate the complex by centrifugation. Recomplexing from butanol and water

purified the product. The amylose complex was stored in butanol and remained soluble in hot water throughout the course of this investigation.

The large-scale procedure is given in Appendix I.

DETERMINATION OF DEGREE OF PURITY OF AMYLOSE

The iodine-binding capacity of pure corn amylose is reported to be between 18 and 20% (125).

The potentiometric method of Bates, French, and Rundle (126) as modified first by Wilson (127-128) and Lansky, et al. (124) was used to estimate the iodine binding capacity of the amylose used in this investigation. The data for three titrations and the resultant calibration curve are presented in Appendix II.

The amylose solutions were prepared for analysis by slowly adding, with stirring, the required amounts of the amylose-butanol dispersion to 90°C. water. Stirring and heating were continued for 5 minutes. The solutions were then filtered under vacuum through a Pyrex M (medium porosity) filter. Butanol was removed by evaporating the solutions under vacuum at 40°C. to less than one-half of their initial volume.

Solution equivalent to about 40 mg. of amylose was pipetted into a 250-ml. beaker; 10 ml. each of 0.5N KI and 0.5N KCl were added along with sufficient water to yield 100 ml. total volume. The solution was titrated potentiometrically at 23.3°C. with iodine reagent (0.20 mg./ml. iodine, 0.05N KCl, 0.05N KI). The reaction was carried out in a water bath and with magnetic stirring. By means of the calibration curve, (Appendix II) the e.m.f. at each increment of iodine addition gave the amount of free iodine in solution, i.e., that iodine not bound to the amylose. Since the total amount of iodine added was known at any increment the amount bound to the amylose at any point could be calculated by difference.

The Iodine Binding Value of a given amylose titration was determined by plotting the amount of free-iodine versus the bound iodine. Appendix III gives the data and plots for these determinations. The Iodine Binding Value was calculated as a percentage by weight of iodine by dividing the maximum bound iodine by the weight of amylose present and multiplying by 100.

PREPARATION OF AMYLOSE SOLUTIONS

Because of the tendency for amylose to retrograde in aqueous solution, amylose solutions for adhesion study were prepared just prior to their use. The following describes the procedure employed:

1. The stock dispersion of the amylose complex in butanol was shaken vigorously to disperse the complex.

2. The desired volume of the dispersion was removed with a large-bore pipet and added to 95°C. distilled water under vigorous mechanical agitation.

3. The dispersion was held at 95°C. for 15 minutes with continuous stirring.

4. The hot amylose solution was filtered under vacuum through a Pyrex-M sintered glass filter. Less than 1% of the amylose was lost as aggregated material.

5. The solution was evaporated under vacuum to less than one-half of its initial volume in order to distill off the butanol.

6. Solutions of amylose were usually prepared so that the concentration after evaporation was below 0.2% and held at 80 to 90°C. in order to avoid severe retrogradation.

7. Following evaporation, the amylose solutions were filtered through a 2500 A. membrane filter in order to remove dust and other particles which may have entered the system. No decrease in amylose concentration was noted which indicated that essentially all of the amylose was molecularly dispersed.

The concentration of all amylose and amylopectin solutions used was measured gravimetrically at 105-110°C. Triplicate determinations checked to within $\pm$ 1% of the mean.

PREPARATION OF AMYLOSE FRACTIONS OF REDUCED MOLECULAR WEIGHT

Three fractions of amylose of reduced molecular weight and broad molecular weight distribution were prepared by acid hydrolysis of whole amylose. The hydrolysis was carried out under helium (to avoid oxidation) at 95°C. and at a pH of 2.7 (0.002N hydrochloric acid). The fractions were isolated at 0.2, 1.0, and 3.0 hours, respectively, and purified by recrystallization with butanol.

The apparatus used was a standard 3-necked, 2-liter round-bottomed flask mounted in a heating mantle and equipped with a magnetic stirrer and a condenser. A gas dispersion tube permitted the constant flow-through of helium gas through the apparatus. The charge consisted of 15 grams of amylose, 473 ml. of 0.01N hydrochloric acid, and sufficient filtered (2500 A. membrane filter) distilled water to yield a total volume of 2500 ml. Samples were removed without interrupting the hydrolysis by siphoning with a water aspirator.

Each fraction was recovered by adding 12% (vol./vol.) of butanol, slowly cooling for 10 hours to allow the amylose-butanol complex to crystallize, and isolating the crystals by centrifugation in a Sharples supercentrifuge. The fractions were stored in butanol as amylose-butanol complexes.

Solutions of the amylose fractions were prepared as needed using the procedure described in the previous section.

PREPARATION OF AMYLOPECTIN AND SOLUTIONS OF AMYLOPECTIN

All of the amylopectin used in this study was isolated from waxy maize (corn) starch, viz. AMIOCA pearl starch from the National Starch and Chemical Corporation. This type of starch is essentially free of amylose.

Two-thousand grams were subjected to five successive extractions with 85% methanol to remove fatty substances. The procedure employed was the same as that used for amylose. Following extraction, the waxy maize amylopectin was air dried and stored in a sealed glass jar.

Solutions of amylopectin were prepared as needed. Two to five grams of the air-dried waxy maize were added slowly with moderate agitation to 2 liters of water at 95 to 98°C. After 30 minutes, the resulting dispersion was very opalescent which indicated the presence of undispersed amylopectin.

Clarification was carried out by continuous centrifugation in a Sharples supercentrifuge at 50,000 r.p.m. (ca. 68,000 g.), followed by pressure filtration of the centrifugate through a 20,000 A. membrane filter. A number of samples, particularly those of low molecular weight, were in addition filtered through 8000 A. and 4500 A. filters. No concentration changes occurred when the solutions were passed through the filters, which indicated that large amylopectin aggregates were not present to a significant degree. This is a reasonable conclusion because amylopectin molecules in solution possess dimensions in the order of magnitude of the pore size of the above filters.

DETERMINATION OF DEGREE OF PURITY OF AMYLOPECTIN

Since amylopectin has negligible ability to bind iodine, the degree of purity of amylopectin was measured by its freedom from amylose by using the potentiometric iodine absorption method described for amylose. The only modification in procedure required for amylopectin was to use 20 times more starch for satisfactory precision.

PREPARATION OF AMYLOPECTIN FRACTIONS OF ALTERED MOLECULAR WEIGHT

As in the case of amylose, it was necessary to prepare amylopectin fractions in a series of decreased molecular weights. Furthermore, a fraction of amylopectin

was prepared which was relatively free of low molecular weight components. Two techniques were utilized, viz., acid hydrolysis and gel filtration.

Acid Hydrolysis

Several studies (129, 130) have shown that the hydrolysis of amylopectin is acid catalyzed and that the first-order reaction rates are constant over a very wide range of degree of hydrolysis. The degree of branching appears to remain constant during hydrolysis unless the amylopectin is hydrolyzed extensively (130).

The procedure used was essentially that of Erlander and French (130) employing potassium acid phthalate buffer, reflux conditions, and a helium atmosphere to avoid oxidation. The procedure is given in Appendix IV.

Gel Filtration

In order to prepare amylopectin fractions of molecular weight lower than that obtained by acid hydrolysis and to prepare a fraction free of low molecular weight amylopectin, the two most highly hydrolyzed amylopectin fractions (70 and 141 hr. hydrolysis, DF-5 and DF-6) were subjected to gel filtration in SEPHADEX* columns. Gel filtration also provided a means for the indirect characterization of the molecular weight distribution of the amylopectin fractions.

As summarized in Table II, seven amylopectin fractions were prepared by gel filtration of the two most highly hydrolyzed amylopectins (70-hr. hydrolyzed DF-5 and 141-hr. hydrolyzed DF-6). One of the Sephadex low molecular weight fractions was hydrolyzed again to yield the lowest molecular weight fraction (DF-5 - IH). Fractions were combined from duplicate runs, concentrated under vacuum, filtered

*SEPHADEX (Pharmacia, Uppsala, Sweden) is a cross-linked dextran comprised of granules which form a swollen, inert, three-dimensional, porous network when suspended in water. The degree of cross-linking controls the pore-size distribution within the granules and hence controls the inclusion or exclusion of particles of a given size when a solution is passed through the column.

TABLE II

AMYLOPECTIN FRACTIONS PREPARED FOR ADHESION EXPERIMENTS

Code	Description	Gel Filtration Characterization[a]
AMP-121	Whole amylopectin	--
DF-6	Whole amylopectin, 141 hr. hydrolyzed	63% was excluded by G-100 Sephadex
DF-6-S-II	DF-6, excluded	Upper 49% mol. wt. fraction of DF-6; excluded by G-100 Sephadex
DF-6-S-III	DF-6, included	Lower 27% mol. wt. fraction of DF-6; included by G-100 Sephadex
DF-5-Ex.	Excluded fraction of 70 hr. hydrolyzed whole amylopectin	Upper 26% mol. wt. fraction of DF-5; excluded by G-75 Sephadex
DF-5-L	High mol. wt. fraction of included DF-5	Included by G-75 Sephadex (highest mol. wt. portion)
DF-5-VL	Low mol. wt. fraction of included DF-5	Included by G-75 Sephadex (lowest mol. wt. portion)
DF-5-IH	Intermediate mol. wt. fraction of DF-5 hydrolyzed 3.0 hr.	Fraction hydrolyzed was that intermediate between the excluded and included fractions of DF-5 on G-75 Sephadex

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[a] Note: Sephadex gel columns are rated nominally to exclude and include various molecular weight fractions of dextran molecules. Branched molecules like amylopectin will not be related closely to the nominal rating of the Sephadex gels. G-100 and G-75 Sephadex gels are rated to exclude mol. wts. above 100,000 and 40,000, respectively.

through membrane filters of 8000 A. pore size, and freeze dried for storage. About 15% (w) of amylopectin was discarded between each of the excluded and included molecular fraction to minimize overlap. The amylopectin solutions were monitored through the columns by spot-plate testing of small samples with iodine. Sodium chloride was used conductimetrically to trace the included molecular fractions. These solutions were desalted on a Sephadex G-25 column.

SOLUTION PROPERTIES OF STARCH FRACTIONS

Light-scattering and viscosity measurements were used to characterize the solution properties of amylose and amylopectin. These techniques provided specific measures of the molecular weight, molecular size, and solution stability of the various starch fractions investigated.

Light Scattering of Amylose and Amylopectin Solutions

All light-scattering work on amylose was carried out using the dissymmetry method. The reader is referred to the literature for the theory of light scattering (131-134). Instrumental details and procedures are given in the manual supplied by the manufacturer. Scattering intensities were determined for 4358 A. light using a Brice-Phoenix Photometer no. 1937 (Phoenix Precision Instrument Company) at angles of 0, 45, 90, and 135°. Diaphragm width was 4 mm. when the small hemioctagonal cell (D-104) was used and 12 mm. in the case of the large cell (D-101). The performance of the apparatus was checked by measurement of absolute turbidity of a 0.50% solution of Cornell standard polystyrene in toluene and also by measuring the molecular weight of Dow Polystyrene B-6.

Clarification of Solutions

The clarification of solutions to remove dust and other foreign particles is extremely critical for the success of light-scattering studies. The presence of small amounts of foreign matter leads to serious errors in molecular weight and

particle size studies because the intensity of scattered light is proportional to the square of the size of the particles. Pressure filtration through 2500 A. membrane filters was found to be the most satisfactory technique for clarification of amylose solutions without a large decrease in concentration. Amylopectin solutions were clarified by centrifugation followed by filtration through membranes (cf. p. 56).

Clarification of Solvent and Cleansing of Cells

Water was clarified by the same porosity filters used for starch solutions. Lowest solvent scattering turbidities of ca. 0.07×10^{-2} were obtained by filtering directly into the scattering cells. Concentration instead of dilution of starch solutions resulted in increased precision of light-scattering measurements.

Filtered, reagent-grade methanol was used for the final rinsing of the scattering cell.

Refractive Index Gradient

The precision of molecular weights determined by light scattering depends greatly on the accurate measurement of the change in refractive index with concentration, (dn/dc), because this term is squared in the equations for calculating absolute turbidity. The dn/dc for amylose solutions was measured with a Rayleigh interferometer (Baird Associates, Cambridge, Mass., Serial no. UA2-19). The procedure and data for the dn/dc determination of amylose are presented in Appendix V. The dn/dc of amylose in water was found to be 0.153 cc./g., which corresponds closely to literature values (135-137). The dn/dc of amylopectin was taken as 0.156 after Erlander and French (137).

Evaluation of Molecular Weight

The procedural details for determining the molecular weight of amylose fractions in water are given in Appendix VI. The results are presented on p. 123. The data are given in Appendix IX.

Stability of Amylose Solutions

Aqueous solutions of amylose were studied by means of light scattering to determine the length of time they could be used in sorption and adhesion experiments before extensive retrogradation occurred. Whole amylose Fractions A and B (see Appendix I, Fig. 30) were examined at room temperature for change of turbidity as a function of time and concentration. An estimate of particle size was made using the P (90°) factor obtained from point dissymmetry measurements and an assumption of a spherical particle shape (133, 134). The results are shown on p. 123.

Viscosity of Amylose Solutions

Viscosity measurements were carried out on both amylose-A and amylose-B in water and in 0.61N potassium hydroxide. These measurements were taken in order to obtain additional information on the solution properties of the amylose used in this study as compared to published information (138, 139) and the light-scattering data.

The viscometer used was of the Ubbelohde type having an efflux time of 160 seconds for distilled water. All determinations were carried out in a water bath at 25.00 ± 0.02°C. Solution concentrations were 0.028 to 0.480 g./100 ml. Specific viscosities were extrapolated to zero concentration to yield the limiting viscosity number (140). No correction was made for shear rate dependency because of the low shear rates employed. The viscosity data and calculations are summarized on p. 193.

MECHANICAL PROPERTIES OF STARCH FRACTIONS

Preparation of Films

A technique was developed for the preparation of amylose and amylopectin films in order that their cohesive strength and certain mechanical properties could be studied in parallel with their bonding behavior with cellophane.

Starch films were prepared by placing 50 ml. of solution of known concentration on a 11.4 x 11.4-cm. area of PLEXIGLAS, evaporating and drying for 40 hours at 23°C. and 50% R.H. The films were cut out with a razor blade and handled with forceps. Films ranging in thickness from 0.32 to 1.67 mils were prepared. Films thinner than 0.3 mil could not be handled without severe damage. Specimens for testing in the transverse-(Z)-direction were cut out with a circular punch die.

Evaluation of Films

The mechanical properties of the starch films in the X-Y and Z-planes were measured as described previously (p. 58). As with the cellophane the starch films had to be abraded with emery powder to attain satisfactory epoxy adhesion.

For testing the films in the X-Y plane, clamping of the specimens was done with zero-span jaws (141) set at 1.27 cm. span. To reduce breakage in the zone of clamping the jaws were lined with cellophane tape and the specimens were mounted in the jaws between pieces of tracing paper. The rate of jaw separation was 0.13 cm./min.

X-Ray Diffraction of Starch Fractions

In order to evaluate the relative crystallinity of several starch fractions as free films and as they existed between cellophane, x-ray diffraction determinations were made.

Laue-type diffraction patterns were obtained using a Norelco unit (Type 12045B) with radiation produced from a copper target and passed through a nickel filter yielding a wavelength of 1.5418 A. The x-ray film was mounted in a special camera designed by Jentzen (142).

The diffraction patterns are presented in Appendix XIII.

The patterns were analyzed quantitatively using the microdensitometer built by Jentzen (142), which permitted the films to be scanned for light transmission continuously along the radii. The minimum and maximum transmission values (corresponding to the first arc and between the first and second arc, respectively), were recorded from the strip charts and converted to optical intensities. The light intensity obtained between the arcs was considered to be the background scatter caused by the less-ordered regions of the starch fractions. The unexposed portions of the films were adjusted to yield 100% transmission. The index of crystallinity was calculated using the following ratio of optical intensities: $(I_{maximum} - I_{minimum})/I_{maximum} \times 100$. Correction was made for the film or polarization factors.

PREPARATION OF BONDS

Two basic approaches were utilized to prepare the bonds between cellophane films using starches or water as adhesives. The initial phases of investigation utilized sorption from aqueous solutions of starch directly onto the cellophane films, followed by drying of pairs of such films in contact. The second manner of bond preparation was an evaporation procedure whereby a given quantity of aqueous starch solution was placed between two cellophane films and permitted to evaporate to effect the cellulose-starch-cellulose bonds. This evaporation technique was used in the major portion of this study and was necessitated by the need for greater amounts of starch in the bonds than could be obtained by sorption from solution.

Bonds made using water as the adhesive between the cellophane films served as controls.

BOND PREPARATION BY SORPTION FROM SOLUTION

A series of cellophane-starch-cellophane film assemblies was prepared by sorbing both amylose and amylopectin from aqueous solutions onto 8-1/2 by 11-inch films of gel and PUD-0 cellophane. About 450 ml. of the desired solution at 0.041 to 0.176% concentration were poured into carefully cleaned 10 by 12-inch enamel or plastic trays. One cellophane sheet was submerged in each solution. Then the tray was heat-sealed in a polyethylene bag and stored at 73 $\pm$ 1°C. for the desired time. Mercuric chloride (10 p.p.m.) was added to the solutions to avoid microbiological action during the long sorption times.

The sorption runs were terminated by washing the films in three successive trays of distilled water followed by a one-half hour soak. In initial experiments, no significant change in amylose concentration could be detected when samples of residual solution were analyzed by the iodine-colorimetric method. No desorption of amylose during soaking could be detected by iodine test.

The cellophane was folded onto itself while still under water, bringing into contact the surfaces which were uppermost during sorption. The assembly was placed on plate glass and pressed into contact with a soft rubber roller at a pressure of about 7 p.s.i. The cellophane-sorbed starch-cellophane system was taped to glass with pressure-sensitive tape uniformly around all four edges and allowed to dry at 23°C. and 50% R.H. The dried assembly was trimmed along the inside edge of the tape with a razor blade and stored at 23°C. and 50% R.H. until tested.

Two groups of control sheets were made using water between the cellophane films. The bonded film specimens prepared in this phase of the study are summarized in Table III.

TABLE III

CELLOPHANE-STARCH-CELLOPHANE BONDS PREPARED BY SORPTION FROM AQUEOUS SOLUTION AT 23 ± 1°C.

Code	Starch Fraction	Concentration Solution, %	pH of Solution	Cellophane Identity	Sorption Time, hr.
26-A	Amylose-B	0.043	6.8	Gel	97.5
26-B	Amylose-B	0.043	6.8	Gel	97.5
31-A	Amylose-B	0.041	6.9	Gel	125.5
31-B	Amylose-B	0.041	3.8[a]	Gel	125.5
31-C	Amylose-B	0.041	3.9[a]	Gel	236
31-D	Amylose-B	0.041	6.9	PUD-0	236
42	Amylose-A	0.176	6.8	Gel	163
41-B	Amylose-B after aging 97.5 hr.	0.043	6.8	PUD-0	184
52	Amylopectin	0.073	6.9	Gel	140

[a] The pH was adjusted with acetic acid.

BOND PREPARATION BY EVAPORATION

The first set of bonds was prepared by using Mayer wire-wound rods to deposit various quantities of amylose solutions of different concentrations. The top edge of wet PUD-0 cellophane was taped to plate glass using pressure-sensitive tape. Immediately following filming with the Mayer rods, the specimens in each case were folded back upon themselves to form an assembly comprised of amylose solution between two pieces of cellophane. This assembly was taped around its perimeter to the glass to permit drying under some restraint to avoid wrinkling. Unless indicated otherwise, all bonds were prepared, dried, and tested at 23°C. and 50% relative humidity. Table IV summarizes the cellulose-amylose-cellulose

bonds prepared by this procedure. The amount of amylose present in this set of bonds was determined by indirect gravimetric means (p. 70).

TABLE IV

AMYLOSE-CELLOPHANE BONDS PREPARED USING MAYER RODS, PUD-O CELLOPHANE, AND AMYLOSE-B

Code	Mayer Rod No.	Amylose Concn., g./l.	Amylose in Final Bond,[a] g./m.^{2}
19-1	(pour-on)	2.15	--
19-2	22	2.15	0.20
19-3	22	2.15	0.20
19-5	12	2.15	0.11
19-6	12	2.15	0.11
19-7	7	2.15	0.08
19-8[b]	22	2.15	0.20
19-9	22	7.03	0.65
19-10	14	7.03	0.39

[a] Approximate only since determined indirectly (p. 69).
[b] Force-dried at 110°C. for 20 minutes.

All other bonds in this study were made by the following procedure. Following standard cleansing, the wet cellulose films (8-1/2 by 11-inches) were placed on plate glass and sprayed with 4500 A. filtered water. The films were smoothed and the surface water removed by means of a soft rubber roller. Each film was then attached on four sides to plate glass using one side of 3M-No. 666 two-sided pressure-sensitive tape. The second side of the tape was then peeled off to expose its sticky surface. A given volume (usually 5 ml.) of freshly prepared starch solution was pipetted onto the wet cellophane, special effort being made to

distribute the liquid uniformly. The tape served as a border to confine the solution. As quickly as possible a second piece of wet cellophane, which also had been sprayed and rolled as above, was placed carefully over the starch solution to coincide with the edges of the first piece of cellophane and pressed into contact with the sticky border of tape holding the first piece of film. After about ten minutes to permit the evaporation of surface water, four more pieces of tape were applied to adhere the edges of the second film to the glass and to more securely bind the entire assembly. The bond assembly was air dried at 23°C. and 50% R.H. This procedure resulted in wrinkle-free bonds of high visible uniformity and transparency. About 90 minutes were required to evaporate the free liquid from the cellophane assembly. The specimens were removed from the glass by cutting just inside the edges of the tape with a razor blade.

A series of bonds was prepared by drying under pressure by the following technique:

1. The procedure was carried out to the point of taping the water-saturated assembly to plate glass.

2. The assembly was exposed to the atmosphere until all of the visible "free" water evaporated (ca. 10 min.).

3. Three 4 by 4-inch layers of dry membrane filler (Millipore VC, 1000 A.) were placed against the cellophane, followed by 300 sheets of Whatman No. 1 filter paper, 4 by 4-inch.

4. This assembly was centered in the Baldwin press and loaded to desired unit pressure, ranging from 25 to 3900 lb./in.^{2}. In the case of the highest pressure set, a 4 by 6 by 2-inch surface-ground steel plate was used for backing instead of the glass. The load was automatically maintained by the press mechanism

until the cellophane was dry. An electric fan was directed between the platens to increase the rate of evaporation. The drying cycle was monitored with an electric hygrometer and required from 15 to 24 hours for completion.

QUANTITATIVE MEASUREMENT OF STARCH IN BONDS

Four methods were used to determine the amount of starch present between the two films of cellophane comprising the various bonds, viz.:

1. Spectrophotometric analysis of the starch present in solution after the starch was dissolved from between the films.

2. Spectrophotometric analysis of the starch in situ.

3. Weight and area measurement of bond assemblies.

4. Calculation based on volume and concentration of starch solution applied and the area of the bond. Each of these procedures is described in the following sections.

Spectrophotometric Analysis of Dissolved Amylose

The most sensitive method available for measuring small concentrations of amylose in water is the iodine-colorimetric technique based on the well-known blue iodine-amylose complex (143).

Calibration curves were prepared relating amylose concentration to absorbance at 625 nm. (wavelength of maximum absorbance) for aqueous amylose solutions prepared under neutral, acidic, and alkaline conditions. The Beckman-DU spectrophotometer and two matched quartz cells (1 cm.) were used throughout this program. Iodine and potassium iodide concentrations were adjusted to 10 and 15 mg./100 ml. of solution, respectively. The blanks contained the same iodine and iodide concentrations but no amylose. The pertinent calibration data and curves are presented in Appendix VII. The neutral amylose solutions followed Lambert-Beers law and gave results of good precision ($\pm$ 0.2 mg./l.) over the full range of 0 to 35 mg./l.

Because the iodine complex was destroyed by alkali and because of the ineffectiveness of acid and alkali in removing amylose quantitatively from the films, the above method was judged unsatisfactory for determining the amylose present on cellophane. The iodine colorimetric procedure was very good, however, for the precise determination of amylose concentrations in dilute neutral aqueous solutions.

Spectrophotometric Analysis of Amylose In Situ

To circumvent the difficulties experienced with the above method and to permit the measurement of large amounts of amylose in a bond, a technique was developed to determine the quantity of amylose present without dissolving the amylose. The procedure was as follows:

Cellophane-amylose-cellophane bond specimens were sampled by cutting out randomly five 0.9 x 4-cm. pieces by means of a razor blade and metal template. The individual pieces were submerged in 0.02% iodine-0.03% potassium iodide solution for one hour in order to permit the full development of the blue coloration of the iodine-amylose complex. The strips were placed in the liquid cell (parallel to cell face) of the Beckman DU spectrophotometer to determine the absorbance of the blue complex. Both the reference and sample cells were filled with the above iodine solution. Two pieces of plain cellophane were placed in the reference cell to comprise the blank. The difference in transmission of light at 625 nm. between the reference (blank-containing) cell and specimen-containing cell was that due to the absorbance of the blue, amylose-iodine complex present in the bond.

The procedure was calibrated by using cellophane containing known amounts of amylose. The specimens were prepared by placing a wet sheet of 8 by 10-inch cellophane film over a film containing a known volume and concentration of amylose. The two films were then dried with the amylose in between in a manner identical to that used for the preparation of specimens for bonding studies.

Appendix VIII presents calibration data obtained for seven separately prepared amylose-cellophane assemblies. Five specimens were cut from each assembly and two spectrophotometric readings were made on opposite sides of each specimen. Very good uniformity of amylose deposition was shown by the relative evenness of the blue coloration and the relatively low coefficients of variation of the absorbance readings. The plot relating absorbance and the amount of amylose between the films followed Lambert-Beers' law.

Film Weight and Area Procedure

In principle it should be possible to determine the amount of starch present in a bond by merely obtaining the difference in weight per unit area of any two films before and after bonding. However, this method generally was not considered to be sufficiently sensitive for this study because: (a) the weight of starch was very small in comparison to the films (e.g., ca. 1:200) and (b) the weight per unit area of the blank films was very difficult to determine accurately due to the washing, wetting, and drying sequence used in preparing the films and bonds. Nevertheless, one set of bonds (Table IV) was measured by a modification of the above approach. When amylose was deposited with Mayer rods, the amount of amylose was measured indirectly by determining the weight of water metered on by the various rods and assuming that dilute amylose would meter similarly. The water deposited was weighed after quickly sealing the cellophane into polyethylene bags. The concentration of the amylose solution was measured which permitted the calculation of the amount of amylose in the bond.

Starch Solution Volume and Concentration Procedure

The total volume of applied starch solution remained confined between the films and facilitated calculation of the amount of starch present in the bonds. Confinement of the solutions was judged complete because the elastomeric adhesive on the tape was wetted very little as revealed by high contact angles. In the case of

amylopectin bonds, this procedure was necessary since the colorimetric procedures based on iodine are rather insensitive because of the low complexing capacity of amylopectin.

AMYLOPECTIN MIGRATION INTO SUBSTRATE

A quantitative measure of the extent of amylopectin diffusion into the two cellophane films during bond formation was necessary in order to characterize the process. The procedure developed was as follows:

1. The bond specimens were conditioned to equilibrium at 50% R.H. and 23°C.

2. Specimen area was determined by direct measurement of its length and width by means of a machinist's rule graduated in 1/100th of an inch and a 14X hand lens. The maximum error in area was estimated to be $\pm$ 0.2% for an 8-cm.^{2} specimen.

3. The specimens were weighed to the nearest 0.1 mg. The weight per unit area is that of the two films plus the total amylopectin.

4. The specimens were immersed in 23°C. water and immediately peeled apart to expose the amylopectin in the bond. The surface amylopectin was removed from both cellophane films by gentle rubbing with a rubber policeman. It is reasonable to assume that the total immersion time of ca. one minute would not permit a significant quantity of amylopectin to diffuse out of the cellophane. Hence, this treatment removed essentially only the amylopectin present between the films and not that diffused into the cellophane substrate.

5. After drying and conditioning at 50% R.H. and 23°C., the surface-washed films were again weighed. The difference in weight between the initial assembly, (3), and the total of the two surface-washed films, (5), is equal to the weight

of bond amylopectin in the system. This weight was then converted to the area basis of one square meter.

6. Treatment of blank (no amylopectin) cellophane-to-cellophane bonds by the above sequence caused no significant changes in weight. Thus, moisture hysteresis effects caused by rewetting and drying of the initial specimens were not significant.

7. The mean weight per unit area of two preroughened cellophane films bonded with water was found to be 76.0 $\pm$ 0.5 g./m.^{2}. Thus, converting the weight and area figures for the amylopectin-bonded specimen into g./m.^{2} and subtracting 76.0 yielded the g./m.^{2} of total amylopectin in the bond system.

8. Subtraction of g./m.^{2} of bond amylopectin (5) from the g./m.^{2} of total amylopectin (7) yielded the g./m.^{2} of diffused amylopectin. The percentage of diffused amylopectin was calculated from these three quantities.

9. In an attempt to evaluate directly the amount of diffused amylopectin in the cellophane, specimens were extracted from 24 to 30 hours in distilled water maintained at 98 to 99°C. in a hot water bath. This technique was not used because it was not feasible to remove all of the amylopectin from within the cellophane.

EVALUATION OF BONDS

STRENGTH OF BONDS

This section describes the equipment and procedures used for evaluating the strength of the cellophane-cellophane bonds. Essentially, this was a modification of the transverse tensile strength (TTS) method for paper developed at The Institute of Paper Chemistry (144-146).

Test Principle

The particular cellophane-cellophane bond assembly to be tested was glued between and perpendicular to the axes of a matching pair of metal cylinders using an epoxy adhesive for the two cellophane-to-metal bonds. Ten such pairs of cylinders were placed in a V-groove alignment jig and subjected axially to a dead-weight load during partial curing of the epoxy adhesive. After sufficient time for total curing, the cylinders were loaded in tension along their axes until failure of the cellophane-starch-cellophane assembly occurred. The ultimate breaking load per unit area of specimen was termed the bond strength.

Please refer to Fig. 2 and 3 for a general view of the apparatus. Paper was used for these photographs, because cellophane did not give sufficient contrast. The details of procedure follow.

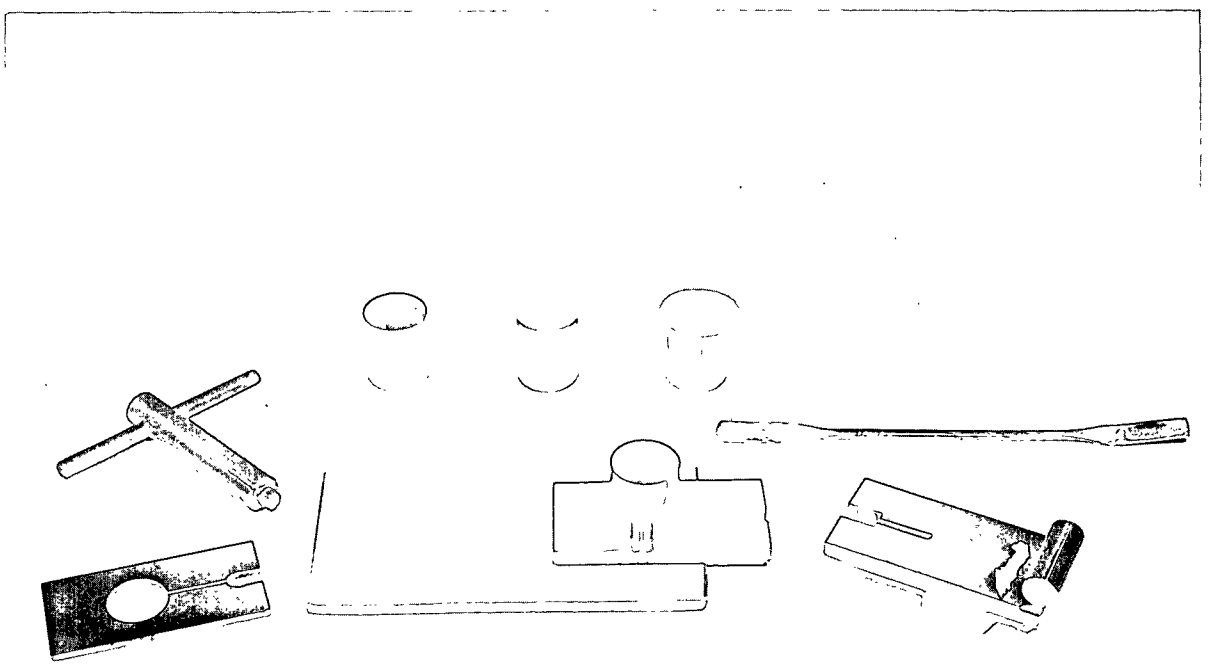


Figure 2. Equipment for Applying Epoxy Adhesive to Test Cylinders

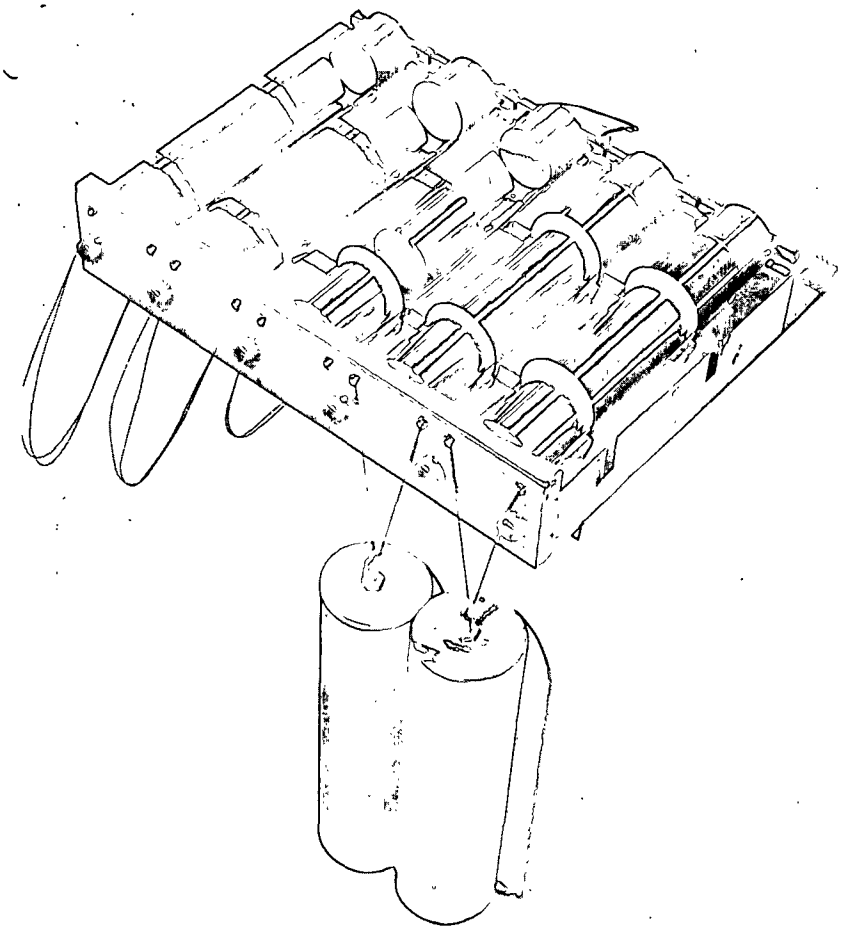


Figure 3. Apparatus for Aligning and Loading of Test Cylinders

Test Cylinders

The test cylinders were made of hardened steel and were surface ground to diameter and height tolerances of ± 0.0002 inch. The test surface edge was sharp and free from burrs and nicks. The cylinder walls were parallel to each other and perpendicular to the test surface. When a cylinder pair was laid face to face in a V-groove of the alignment jig, the match was so good that the junction of the cylinder pair was scarcely visible and was undetectable by touch.

Twenty pairs of cylinders were built by the Fox River Tool Company, Menasha. Their diameter was 0.9903 inch and their height 1.2470 inches. Each cylinder was drilled and tapped to 3/8 inch on one end to permit attachment to the stud of the cylinder holder of the tensile testing apparatus. Cylinders of other sizes were also used during some of the initial tests. Perpendicularity of the thread tap to the cylinder face was checked on a lathe with a dial micrometer.

Adhesive Application

The epoxy adhesive used was Epon 907 (Shell Chemical Company, Pittsburg, California). A weight ratio of 1.00:0.60 of Parts A (resin) and B (activator) was placed on a glass plate and mixed thoroughly with a spatula. Curing of this adhesive commenced at room temperature with the mixing of these two components. A given mix was used within 10 to 30 minutes to avoid reduced adhesion which occurred at longer time intervals, as evidenced by peel-failure and low strength of cellophane-epoxy bonds.

A predetermined film thickness (usually 3.4 mils) was applied by use of a filming plate and a metering rod. The filming plate was placed horizontally onto plate glass. A square of aluminum foil of desired thickness was centered within the hole of the filming plate. A cam-lever was used in the slot of the filming plate to increase the diameter of the hole so that the test cylinder to

be filmed could be slipped into the hole. The foil served to recess the plane of the cylinder face below that of the lower plane of the filming plate. The cylinder was clamped tightly in this fixed position by reducing the diameter of the hole by turning the cam-lever. The assembly of cylinder and filming plate was inverted to expose the cylinder surface and the bottom of the plate. An excess of epoxy adhesive was placed on the plate in front of the cylinder surface and a surface-ground metal metering rod was drawn along the length of the plate to meter a film onto the recessed cylinder face. The thickness of film deposited on the face corresponded to the depth of recess of the test cylinder below the plane of the filming plate. Then the cam-lever was again twisted in the notch to release the cylinder from the filming plate. The plate was rinsed in methanol, and the above procedure repeated for as many cylinders as required.

Cylinder Assembly, Alignment, and Loading

The cellophane samples to be tested were cut into oversized circles with a die. Each circle was then assembled between two of the epoxy-filmed cylinders as follows: The cellophane was placed on a flat surface such as plate glass and dusted with a fine brush. One filmed cylinder was carefully placed flatly onto the cellophane. The cellophane adhered to the epoxy film when the cylinder was lifted. The exposed cellophane surface was dusted and the cylinder placed horizontally into the V-groove of the alignment jig. Another epoxy-filmed cylinder was slid carefully along the same V-groove into contact with the exposed cellophane surface, thus creating an assembly of two cylinders, an epoxy film on each cylinder, and a cellophane-cellophane bond specimen positioned between the two epoxy films.

Ten pairs of cylinders were arranged in the alignment jig at one time as shown in Fig. 3, utilizing one V-groove for two pairs of cylinders. Each V-groove had two 1/4-inch right-angle gaps positioned to coincide with the zones of bonding.

This permitted the cellophane specimen to be larger than the cylinder diameter and also allowed a small bead of epoxy to flow out of the joint during curing.

The cylinders in each of the five grooves were dead-weight loaded to either 808 or 404 g./cm.^{2} axially by means of separate 1-inch diameter loading cylinders. Weights were attached to the loading cylinder by means of two nylon threads which ran parallel to and along both sides of the test cylinders and passed through the face plate of the alignment jig which was perpendicular to the plane of the V-grooves. In this manner, the test cylinders were forced together in controlled fashion to yield test assemblies having reproducible epoxy film thicknesses.

Curing of Adhesive

The cylinders were held under load in the alignment jig for two to three hours, during which period the epoxy had cured to the point where the cylinder pairs could be removed from the jig. Curing conditions are discussed on p. 83.

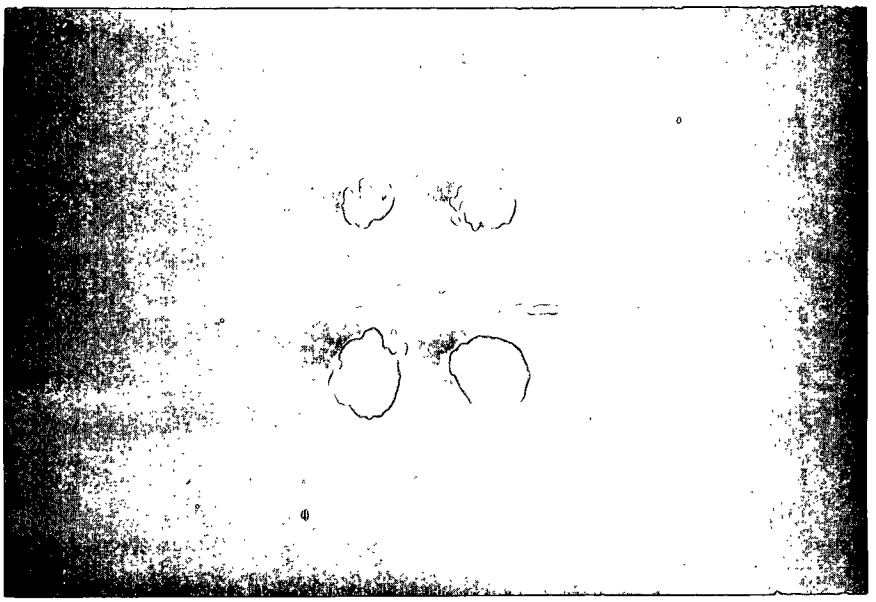
Testing of Strength of Bonds

The assemblies prepared above were tested in tension on a Baldwin-Southwark Universal tester. Special precautions were taken to insure that the load applied to the cellophane bonds was normal to the plane of their surface. Each pair of test cylinders containing one test specimen was carefully screwed onto an upper and a lower test-cylinder holder. These two holders were positioned on the upper and lower crossheads of the Baldwin prior to a series of tests. Each cylinder holder was connected to the Baldwin crosshead through a ball-and-socket universal joint. This insured the application of loads through the axes of the cylinder holders, regardless of the alignment of the cylinder holders in the Baldwin. Alignment on the Baldwin was checked periodically with a plumb-line and spirit level. The standard loading rate was 0.13 cm./min., or ca. 900 kg./min.

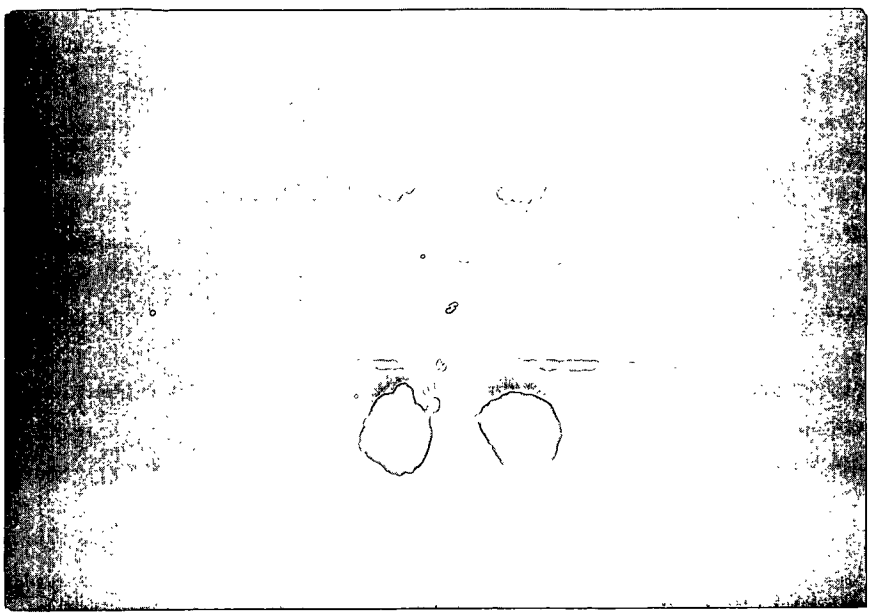
The cylinder holders were carefully machined to insure that (1) the studs upon which the test cylinders were to be screwed were parallel to the axes of the cylinder holders, and (2) the surfaces against which the test cylinders were to be screwed were normal to the axes of the holders. The perpendicular alignment of the faces of the test cylinders on the cylinder holders was accurate to within 0.0001 inch when checked with a dial micrometer during rotation on a lathe.

The effective test area of the specimens was determined after failure by micrometric measurement of the diameter of the resin bead on the cylinder faces. Two readings at right angles were averaged for each cylinder and the smallest diameter cylinder of the test pair was used for calculating the effective test area. The diameter range was 1.015 to 1.030 inches.

High-speed motion pictures were taken during three separate tension loading cycles of amylose-cellophane bonds. The objectives were to check the alignment of the apparatus and test cylinders and to learn something about the nature of the failure. The sequences were photographed at speeds ranging from 6000 to 9000 frames per second using Tri-X negative 16 mm. film in a Fairchild camera. The test cylinders were covered with black velour paper so that the zone of bonding would contrast clearly with the black background employed. The bonds were loaded at the rate of 9,500 kg./min. The two photographs of Fig. 4 are enlargements of two consecutive frames taken during failure of a bond. The horizontal white areas are the side views of the epoxy adhesive present on each cylinder. The top picture is the first frame in the sequence where separation of the two epoxy layer was evident. The bottom picture shows the gross separation of the bond which occurred in 1.2×10^{-4} seconds. Careful study of the films and photographs revealed that the faces of the cylinders remained parallel during loading and immediately after failure. This indicates that direct axial loading was being applied to the bonds and that little, if any, force couple existed.



First Frame Where Bond Failure Could Be Detected



Next Frame in Bond Failure Sequence

Figure 4. Frames from High-Speed Motion Pictures Showing Bond Failure.
Speed: 9000 Frames per Second
These Two Frames Are ca. 1.2×10^{-4} Seconds Apart

Cylinder Cleaning and Storing

The hardened epoxy was loosened by one hour of soaking in methanol. The cylinders were stored in a vacuum desiccator over Drierite to reduce corrosion. The cylinder faces were rinsed in reagent methanol and dried just prior to filming to insure a clean surface for good epoxy-to-metal bonding.

Mechanical Variables of Procedure

Trimming of Specimens

Initial experiments were carried out on cylinder assemblies which were trimmed with a razor blade to remove the exuded epoxy and excess cellophane, and to obtain a constant cross-sectional area for testing. Five sets of comparisons (Table V) showed highly significant decreases in apparent bond strength as a result of trimming of the specimens. Therefore, all subsequent evaluations of bond strength were made without trimming the specimens.

Size of Punch Used for Sampling

Another variable affecting effective bond strength was the size of the circular punch employed to cut the test specimens from the cellophane film bond assemblies. The data in Table VI showed that the use of a 1.0-inch punch resulted in a 25 to 30% reduction of trimmed-specimen bonding strength as compared to the 1.25-inch punch. Apparently, the 1.0-inch sample punch damaged the periphery of the bonded zone between the films and created weak points within the test area. The use of a 1.125-inch punch yielded the same values as the 1.25-inch punch. All subsequent sampling was carried out with the 1.25-inch punch.

Rate of Loading

Fifteen specimens were cut from one cellophane-amylose-cellophane assembly, randomized, and tested in groups of five at three rates of loading. The data summarized in Table VII indicated no significant differences in bond strength for

TABLE V

EFFECT OF TRIMMING CYLINDER ASSEMBLIES ON BOND STRENGTH[a]

Code	Trimmed[b]	Type of Bond	Number of Tests	Apparent Adhesion, kg./cm.^{2}	90% Confidence Range of Mean, kg./cm.^{2}	Standard Deviation, kg./cm.^{2}	Level of Significance, t-test	Coefficient of Variation, c.v., %
B-26	No	Amylose	5	104.2	±8.7	11.8		11.4
							0.02	
	Yes	Amylose	8	87.1	±5.6	9.6		11.0
95-A	No	Water	9	86.3	±3.6	6.6		7.7
							0.01	
	Yes	Water	5	77.2	±2.2	3.1		4.0
106-B	No	Water	10	87.2	±3.8	7.2		9.1
							0.001	
	Yes (after 24 hours)	Water	3	55.0	±2.4	1.4		4.5
19-2-3-8	No	Amylose	5	145.1	±8.5	11.5		8.0
							0.001	
	Yes		15	105.4	±5.3	12.5		11.9
19-6	No	Amylose		133.3	±0.8	0.9		0.7
							0.001	
	Yes					--		8.2

[a]

[b]All samples prepared with 1.0 mil PUD-O cellophane.
Trimming carried out after 2 to 3 hours of cure time at 23°C. except where noted.

TABLE VI

EFFECT OF SIZE OF SAMPLING PUNCH ON CELLOPHANE-WATER-CELLOPHANE BOND STRENGTH[a]

Set Code	Cellophane	Ethanol Wash	Diameter of Sampling Punch, in.	Number of Tests	Apparent Adhesion, kg./cm.^{2}	Decrease Due to 1.0-in. Punch, %
82	PUD-O	Yes	1.25	8	85.2	
			1.00	5	62.6	26.5
82	Gel	Yes	1.25	4	115.8	
			1.00	5	80.0	30.7
82	Gel	No	1.25	16	88.4	
			1.00	15	63.5	28.1

[a] All bonds prepared from water with or without an ethanol wash. All specimens were trimmed after 2-3 hours of cure time of epoxy resin.

TABLE VII

EFFECT OF RATE OF LOADING ON STRENGTH OF AMYLOSE-CELLOPHANE BONDS[a]

Loading rate, kg./min.	Apparent Adhesion, lb./in.^{2} 227	907	2270
	1529	1590	1655
	1560	1532	1614
	1544	1453	1717
	1767	1663	1671
	1708	1673	1618
Mean, lb./in.^{2}	1622	1582	1655
kg./cm.^{2}	114.0	111.2	116.3
Coefficient of variation, c.v., %	6.3	6.0	2.6
95% Confidence limits	±6.2	±5.8	±2.6

[a] Specimen: 41-B, PUD-O cellophane bonded with amylose-B sorbed from solution.

rates of loading of 227, 907, and 2270 kg./min. Thus, all tests carried out at the standard rate of 907 kg./min. were considered insensitive to any small variations in rate of loading which might occur during testing.

In later phases of the study a series of amylose-cellophane bonds were subjected to a wider range of loading rate; viz., 45, 907, and 27,200 kg./min. Fifteen specimens in each group were analyzed and the data are presented in Table VIII. The lower two rates gave almost identical results, whereas the highest rate gave a mean bond strength about 10% higher.

Curing Conditions of Epoxy Adhesive

The following factors which may affect the mechanical properties of the test assembly were studied.

Curing temperature and time. Temperature during curing was raised in a number of instances to reduce the time required to set the resin and to increase adhesion. This was found necessary in the case of bond strengths in excess of 160 kg./cm.^{2} to prevent the epoxy-to-cellophane bond from failing before the starch-to-cellophane. The data in Table IX show that heat curing at 60°C. for 2 hours does not significantly change the strength of cellophane bonds made with amylose, amylopectin, or water. In addition, the peeling of the cellophane specimen from the cylinder during failure was eliminated. Curing cycles were standardized to 2 hours at 60°C., along with a precure of 4 to 6 hours at 23°C. and postcure reconditioning of the specimens at 23°C. and 50% R.H. for at least 6 hours.

Epoxy film thickness. When 3.4 mils (86 μm.) of epoxy was applied to each cylinder and the pairs loaded with 808 g./cm.^{2}, 1.6 mils (41 μm.) of epoxy was found on each cylinder following curing and testing. When 404 g./cm.^{2} was used for loading, 2.0 mils of epoxy remained. The film thicknesses were measured with a dial micrometer (Federal, 0.0001-inch graduations, 3/16-inch diameter foot)

TABLE VIII

EFFECT OF RATE OF LOADING ON STRENGTH OF AMYLOSE-CELLOPHANE BONDS[a]

Loading rate, kg./min.	Bond Strength, lb.		
	45	907	27,200
	3520	3630	3810
	3850	3910	3970
	3960	3670	4270
	4290	4110	4530
	4060	4030	4110
	3420	3620	3430
	3010	2910	4530
	3350	3110	4710
	4020	4030	3880
	3020	3220	3360
	3210	3190	3220
	3420	3550	4240
	3150	3490	3850
	3790	3350	4000
	3410	3890	4140
Mean, lb.	3564	3581	3936
Mean, lb./in.^{2}	4300	4320	4760
Mean, kg./cm.^{2}	302	303	335

[a] Bonds were coded 47-2203 and contained 1.0 g./m.^{2} of amylose.

TABLE IX

EFFECT OF CURING CONDITIONS ON CELLOPHANE BOND STRENGTH

Code	Bonding Agent	Hr. at 23°C.	Heat Cure Temp., °C.	Heat Cure Time, hr.	Hr. at 23°C. for Reconditioning	Number of Tests	Effective Adhesion, kg./cm.^{2}
118-C	Water	32	--	--	--	5	92.5
		8	80	2	6	5	82.5
		8	80	1	6	5	93.3
32-2131-A	Amylose	25	--	--	--	5	156.6
		6	60	2	10	5	161.2
32-2131-E	Amylose	25	--	--	--	5	158.0
		6	60	2	10	5	154.8
52-2131-A_1	Amylopectin	24	--	--	--	2	166.2
		4	60	2	6	4	170.2
52-2131-A_2	Amylopectin	24	--	--	--	2	169.1
		4	60	2	6	4	177.0
52-2131-A_3	Amylopectin	24	--	--	--	2	170.9
		4	60	2	6	4	162.2
52-2131-A_4	Amylopectin	24	--	--	--	2	175.1
		4	60	2	6	4	176.4
52-2131-C_1	Amylopectin	24	--	--	--	2	145.0
		4	60	2	6	4	175.0
52-2131-C_2	Amylopectin	24	--	--	--	2	174.5
		4	60	2	6	4	176.3
52-2131-C_3	Amylopectin	24	--	--	--	2	168.8
		4	60	2	6	4	172.8

following their removal from the faces of the test cylinders with methanol. Individual measurements on a given film seldom varied more than ± 0.1 mil from the mean.

No pattern was observed between epoxy film thickness and cellophane film to film bonding strength; i.e., in any given set of determinations, high or low test values could not be related to thick or thin epoxy films. It was concluded that the very small range of variations in epoxy film thickness resulting from the use of 3.4 mils of initial resin and 404 g./cm.^{2} loading had no observable effect on cellophane adhesion values.

Specimen Roughening

At testing loads in excess of about 160 kg./cm.^{2}, considerable failure of cellophane-to-epoxy bonds was observed accompanied by peel-type failure at the interface. Gentle abrasion with dry emery of the cellophane prior to bond and cylinder preparation resulted in ultimate stresses of over 300 kg./cm.^{2} and totally eliminated peel-type failure at the epoxy-cellophane interface.

Specimen Origin

A 4-1/2 by 7-inch cellophane-to-cellophane assembly bonded from water was sampled randomly in 15 positions and tested to determine if bonding strength was a function of specimen position. An analysis of sample location and bonding strengths showed no pattern of bias in strength due to specimen position. This supported the viewpoint that differential sheet shrinkage was not a disturbing influence on bonding between the two cellophane films.

CHARACTERIZATION OF BONDS

Microtome Cross-Sectioning and Photomicrography of Bonds

In order to determine the nature and degree of penetration of starch in the various cellophane-starch bonds, cross sections and photomicrographs were prepared.

Selected bonds were first embedded in catalyzed fluid butyl methacrylate which was then polymerized with oven heat. Bond sections of 20 μm. thickness were cut perpendicular to the plane of the films using a sliding microtome. An iodine-water-glycerol solution was used to develop coloration of the starch. Photomicrographs were taken at 110X and 210X to record the results. Figure 5 depicts a typical stained cross section of an amylose-cellophane bond assembly. The excellent contact of the two cellophane films and the amylose adhesive (dark, center line) is evident.

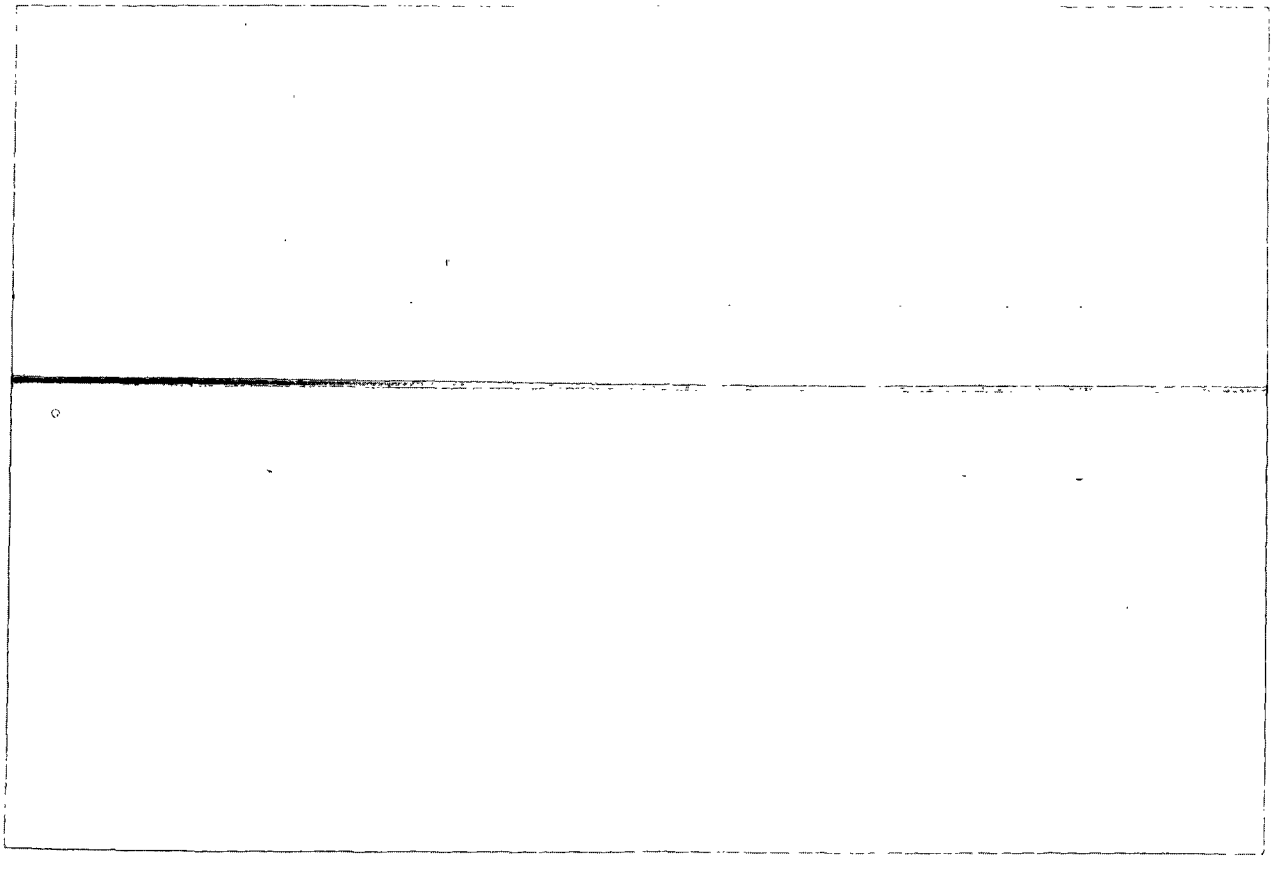


Figure 5. Photomicrograph of Cross Section of Cellophane-Amylose-Cellophane Bond. Dark Area in Center is Amylose

Magnification: 210X
Section Thickness: 20 μm.
Stain: I-KI
Amylose: 70,000 $\underline{M}_{\underline{W}}$, 3.3 g./m.^{2}

Nature of Bond Failure

Following bond failure, each test cylinder normally retained one of the cellophane films which comprised the bond. The two cellophane surfaces were examined for the extent of cohesive failure by noting the discontinuous nature of the films in those regions. The percentage of cohesive failure was estimated visually on an area basis, expressed as that of the total surface area of the bond. Observations of any unusual failure patterns were noted, especially if they appeared to be related to anomalous strength values.

The amount of starch was too small to be detected visually unless the failure zones were first placed in dilute iodine-potassium iodide solution to develop the colors of the starch-iodine-complexes. In the cases of the specimens bonded with amylose and high molecular weight amylopectin the color was relatively permanent and the nature of the fracture patterns and the location of the amylose could be evaluated. However, the low molecular weight amylopectin fractions were too soluble to permit ready evaluation.

Photographs of some of the bond failure zones were taken to provide a record of their characteristics. A fixed focus camera using Polaroid film (Pola Pan 200, Type 52, 4 by 5 inches) and providing magnification of 3 diameters was used. The photographs were made using low angle (5°) illumination in order to accentuate the three-dimensional nature of the surfaces of the ruptured bonds.

The nature of typical rupture surfaces is presented in Fig. 6 which is the top view of a pair of test cylinders after failure of a typical, strong cellophane-amylopectin-cellophane bond. One film of cellophane remains on each of the test cylinders. The white areas are the epoxy adhesive showing through the transparent regions of the cellophane films. The black regions are amylopectin which has been stained with iodine. The cohesive failure of the cellophane is evident on the right

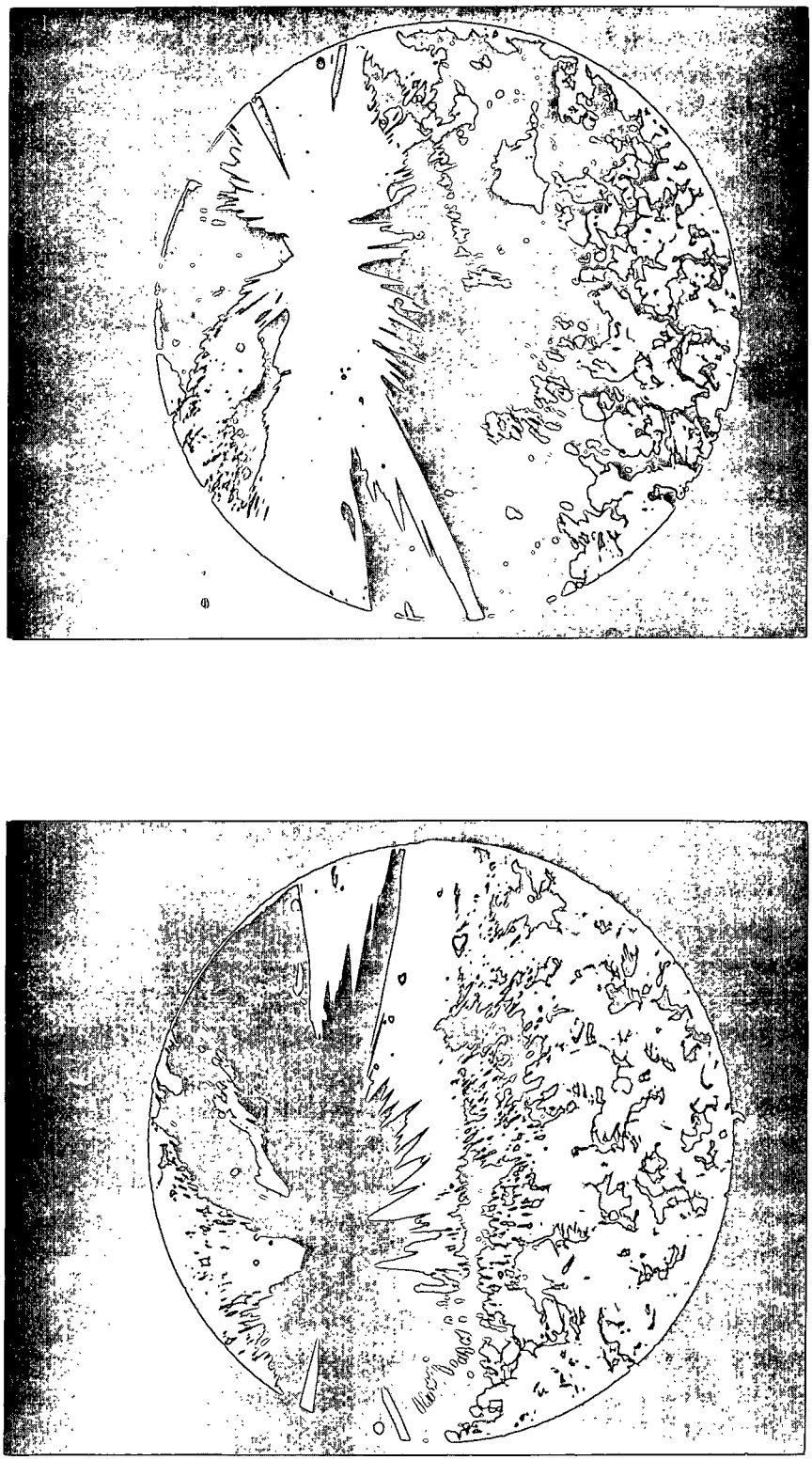


Figure 6. Top View of the Two Failure Zones Resulting from Rupture of a Typical, Strong Cellophane-Amylopectin-Cellophane Bond; 0.82 g./m.^{2} Amylopectin

Magnification: 3X

one-third of each surface. This cellophane failure is restricted toward its surface; at no time was the cohesive failure transmitted through its entire thickness. It should be noted that the fracture patterns of the amylopectin and cellophane on the two cylinders may be matched by a 180° rotation of either picture toward the other, out of the plane of the page.

EXPERIMENTAL RESULTS AND DISCUSSION

INTRODUCTION

The balance of this discussion is devoted to the presentation and discussion of the experimental results. Adhesion in three systems is examined, viz.: (a) cellophane-water, (b) cellophane-amylose, and (c) cellophane-amylopectin.

It should be stressed that the values of adhesion determined in this experimental work are not necessarily related to theoretical, thermodynamic adhesion as calculated from interfacial energies. The data obtained for the destructive testing of the cellophane-starch-cellophane bonds is termed the effective adhesion and depends not only on the various thermodynamic parameters, but also on rheological and mechanical considerations of the adherends and adhesives and on the testing geometry.

ADHESION OF CELLOPHANE WITH WATER

Because all of the starch fractions were applied to the cellulose adherend from aqueous solution, it was necessary to determine the behavior of water alone in the adhesion of cellophane. This would permit an evaluation of the separate mechanisms of behavior of water and starch.

SURFACE CONTAMINATION OF CELLOPHANE AND ADHESION WITH WATER

It was possible that wood extractives as well as other organic impurities could remain or be deposited on the cellophane surface during the manufacturing process. This would serve to reduce the free surface energy of the cellophane and thereby to hinder the wetting and penetration of aqueous adhesives. A study was made to determine if cellophane-to-cellophane adhesion upon drying from water was affected by the solvent cleansing of the films prior to bond formation. The

control sheets were bonded after soaking the cellophane films only in distilled water.

Table X summarizes the effect of surface cleansing of cellophane on adhesion. In spite of some scatter from sheet to sheet, coefficients of variation averaged eleven percent or less in all instances. Surface contamination of the cellophane was indicated by the increase in effective adhesion (in kg./cm.^{2}) from ca. 80 for no cleansing to ca. 88 for ethanol cleansing, and to ca. 95 for combined carbon tetrachloride-ethanol and trichloroethylene vapor cleansing. This, of course, does not prove that all the contamination had been removed. Possibly, the solvents themselves may remain as trace residuals on the surface of the cellophane, although this is unlikely because the solvents were applied in a sequence of increasing polarity. The fact that adhesion was increased by about 19% indicates that surface contamination had been reduced significantly. Consequently, all cellophane films used in this study were precleansed by the carbon tetrachloride-ethanol-water sequence.

TABLE X

EFFECT OF SOLVENT CLEANSING OF CELLOPHANE ON CELLOPHANE-CELLOPHANE ADHESION ON DRYING FROM WATER[a]

Pretreatment of Cellophane	Number of Bonds Evaluated	No. of Tests	Effective Adhesion, kg./cm.^{2}	Coefficient of Variation, %
None	1	5	80.5	6.7
Ethanol	6	49	87.5	9.6
Carbon tetrachloride and ethanol	4	40	95.1	11.1
Carbon tetrachloride, ethanol, and 7-1/2% sodium hydroxide	2	14	90.5	4.9
Carbon tetrachloride vapor only	1	10	82.6	4.4
Trichloroethylene vapor only	1	15	93.2	5.1

[a] Cellophane was PUD-0 type.

Figure 7 presents a threefold enlargement of the appearance of a typical zone of failure of a cellophane bond formed with water. Examination of the cellophane surfaces after bond failure indicated no cohesive failure of the cellophane, i.e., failure appeared purely adhesive in nature.

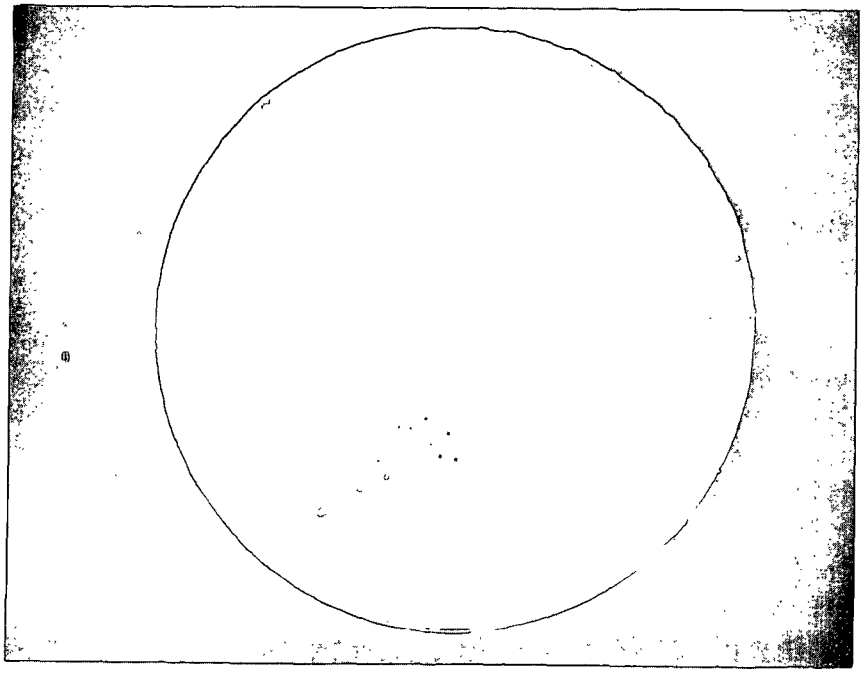


Figure 7. Photograph of Zone of Failure of a Cellophane-Water-Cellophane Bond. One Film is Shown Attached to Metal Test Cylinder. Not Shown Is the Other Film of the Original Bond Attached to the Other Cylinder of the Joint Assembly. Magnification: 3X

Effective adhesion decreased about 5% when the cleansing sequence ending with 7-1/2% sodium hydroxide was used (Table X). A reason for this behavior is that the extensive, alkali swelling of the cellophane created a large increase in the size of surface irregularities; thus, any possible gains in the availability of surface hydroxyl groups and film plasticization were offset by the greater difficulty of approach of surfaces on a molecular scale.

SURFACE CONFIGURATION OF CELLOPHANE AND ADHESION WITH WATER

Both sides of the cellophane surfaces were characterized by use of the Brush surface analyzer and by electron photomicrographs of surface replicas. The results of the Brush profile study are summarized in Table XI and a typical photomicrograph shown in Fig. 8. It is evident that the surface ridges of the cellophane specimens were directional. The mean magnitude of the irregularities was 46 to 127% higher when the stylus travel was in the cross-machine direction (at right angles to the direction of extrusion of the film) than in the machine direction.

The effect of the directional and two-sided nature of the surface irregularities of cellophane on the effective adhesion between cellophane was studied by bonding pairs of PUD-0 cellophane film with water in such a manner that the machine directions of the juxtaposed films were either parallel or perpendicular to each other. Both sides of the cellophane were also evaluated. The results are summarized in Table XII.

It is concluded that the orientation of the surface irregularities of the substrate significantly influenced the degree of surface-to-surface contact of the cellophane films and hence affected the level of adhesion which could be achieved. It is evident that surface-to-surface "fit" of the films was favored by parallel orientation of the pattern of surface irregularities of the two surfaces involved.

Because of the effects of directionality on adhesion, all bonds in the work which follows were made with the films arranged in parallel and the "up" sides in contact.

TABLE XI

BRUSH SURFACE ANALYSIS OF SURFACE CONFIGURATION OF WATER-SWOLLEN AND DRIED CELLOPHANE

Cellophane Specimens and Their Code		Side (as stored)	Direction of Stylus Travel[a]		Average Deviation, d_{av}[b] microinches	A.	Total No. of Deviations Greater than 1480 A.
PUD-0	M-4	Up	MD		2.74	696	28
	M-5				2.23	566	26
	M-6				2.23	566	26
				mean	2.40	610	27
PUD-0	C-4	Up	CD		3.57	907	75
	C-5				3.26	828	68
	C-6				3.69	937	82
				mean	3.51	892	75
PUD-0	M-4	Down	MD		1.96	498	36
	M-5				3.35	851	52
	M-6				2.69	683	48
				mean	2.67	678	45
PUD-0	C-4	Down	CD		4.72	1199	112
	C-5				3.80	965	110
	C-6				4.74	1204	117
				mean	4.42	1120	113
PUD-0	M-7	Up	MD		1.74	442	20
	M-8				2.32	589	32
	M-9				2.27	577	24
				mean	2.11	536	26
PUD-0	C-7	Up	CD		5.09	1293	125
	C-8				3.83	973	105
	C-9				5.08	1290	132
	C-10				6.22	1580	141
	C-11				3.71	942	101
				mean	4.79	1217	121

[a] MD and CD refer to machine direction and cross direction, respectively.

[b] Mean of deviation above and below the reference plane of the trace. Sixty readings taken during 3.0 cm. of lateral stylus motion on cellophane.

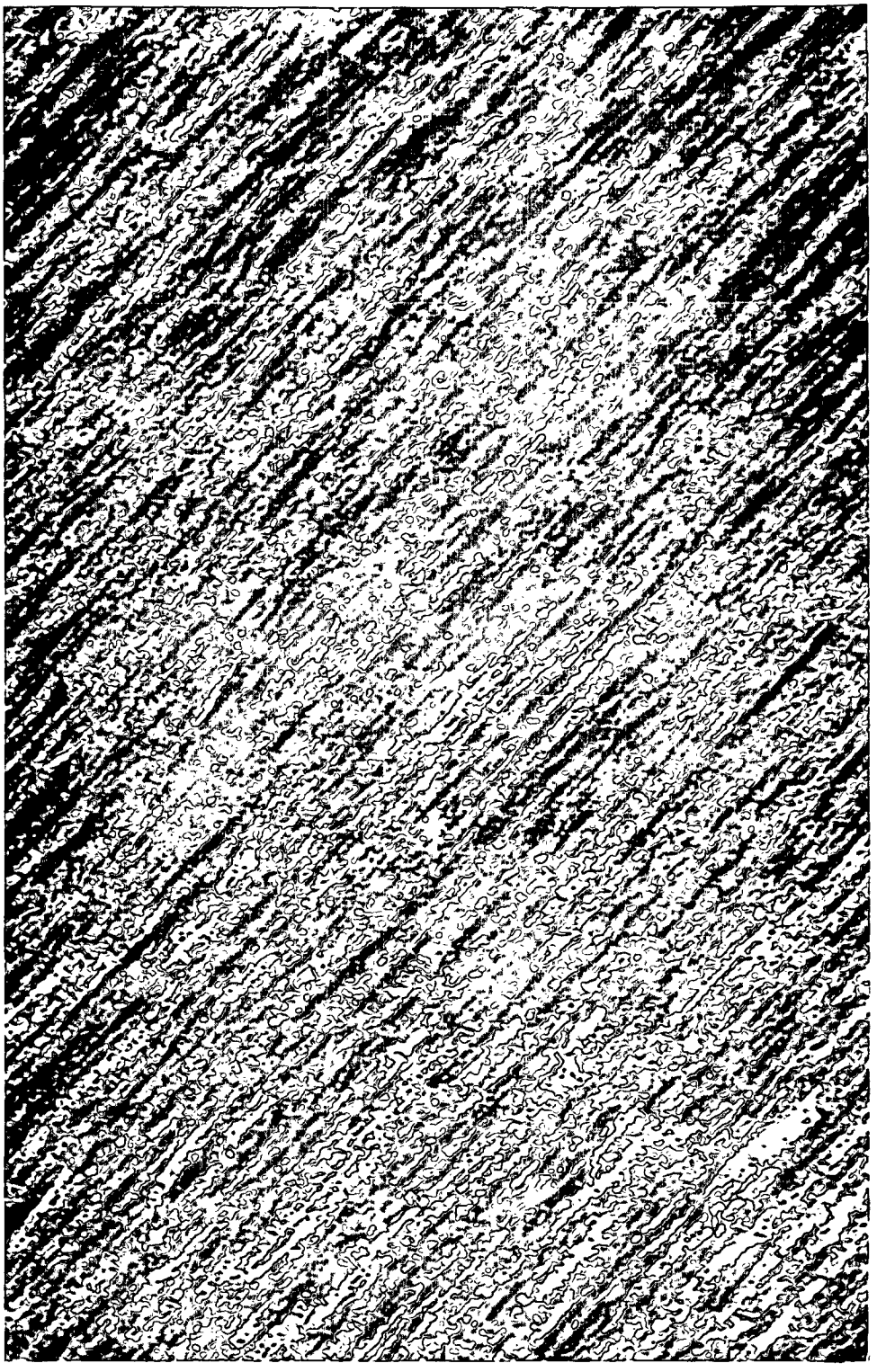


Figure 8. Electron Photomicrograph of PUD-0 Cellophane-"Down" Surface Replica. Magnification: 99,000X

TABLE XII

EFFECT OF DIRECTIONALITY OF SURFACE ON CELLOPHANE ADHESION FROM WATER

Code	Relative Orientation of the Machine Direction of the Two Films	Sides of Films in Contact	No. of Tests	Effective Adhesion, kg./cm.^{2}	Standard Deviation of Mean, kg./cm.^{2}	90% Confidence Range of Mean, kg./cm.^{2}
118-A	Parallel	Up	5	88.9	2.7	± 4.5
118-B	Perpendicular	Up	5	76.9	3.8	± 6.2
118-C	Parallel	Down	15	92.0	3.3	± 5.5
118-D	Perpendicular	Down	5	80.0	2.9	± 4.7

Comparison of Means: Student's t-Test

118-A vs. 118-B--significant difference at 0.05 level

118-C vs. 118-D--significant difference at 0.02 level

SURFACE ABRASION AND DRYING UNDER PRESSURE: EFFECT ON ADHESION OF CELLOPHANE WITH WATER

Since cellophane bonded from water was used throughout this study as a control, the question arose as to the maximum adhesion possible for this system. The above results indicated that cellophane-to-cellophane adhesion from water was primarily dependent on the extent of surface-to-surface contact, provided that the cellophane surfaces had been cleaned.

Surface Abrasion

Results of initial abrasion experiments are presented in Table XIII. The abrasion of the PUD-0 cellophane films was carried out with emery dust as described previously. The films were solvent cleansed by the standard procedure except where indicated. Set G-59 was prepared by removing 3.8 μm. of the cellophane surface with a surface grinder. A 60-grit wheel was found to be the most satisfactory,

since finer grit wheels collected cellophane particles and caused tearing of the films.

TABLE XIII

EFFECT OF ABRADING CELLOPHANE SURFACES ON THEIR ADHESION FROM WATER

Assembly Code	Abraded	Solvent Cleansed[b]	Effective Adhesion, kg./cm.^{2}	Change in Adhesion Compared to Control, %
G-60A	Yes[a]	Yes	135.7	+62
	No	Yes	83.5	+14
G-60-C	Yes[a]	Yes	142.8	+77
	No	Yes	80.5	+11
G-60-B	Yes[a]	No	123.2	+76
	No	No	69.9 (control)	--
G-53-J-0	Yes[c]	Yes	108.0	+38
G-59	Yes[d]	Yes	47.2	-23

[a] Moderate abrasion (260 strokes) to uniform opalescence using 303 emery dust.
[b] Standard CCl_4, ethanol, water bath and spray sequence.
[c] Abraded very lightly (30 strokes) with 303 emery dust.
[d] Prepared by means of surface grinding to a depth of 3.8 μm. with a 60-grit wheel.

In all instances where the bonded cellophane surfaces were preabraded, the effective adhesion was markedly higher (62 to 76%) than that of the corresponding unabraded controls. The bond strength of the mildly abraded specimens (G-53) was not as high as that of those more thoroughly abraded but was significantly above that of unabraded cellophane-cellophane bonds.

In contrast, the surface-ground cellophane surfaces exhibited very low effective adhesion, even considerably below that obtained for the unabraded controls. Microscopic examination of these cellophane surfaces under low angle illumination revealed gross ridges in the direction of grinding. Furthermore, optical clarity of the bonded zone was not achieved on drying. These two observations were

indicative of low surface-to-surface contact of the films and provide a possible explanation of the relatively poor adhesion obtained.

It is evident that the nature of the roughening is critical and that, even though roughening always increases the surface area of a solid, it is of no use in improving surface-to-surface contact if large "hills" and "valleys" exist which reduce net contact.

It is obvious from the data of Table XIII that abrasion (by itself) was considerably more efficacious than solvent cleansing (by itself) in increasing cellophane adhesion from water. However, solvent cleansing of abraded cellophane specimens significantly increased effective adhesion. Thus, it may be concluded that the abrasion of cellophane markedly increased cellophane adhesion from water, in spite of the fact that abrasion was not fully effective in removing surface contaminants. Thus, surface contamination in these experiments was not as critical a factor in reducing adhesion as was the physical structure and conformation of the cellulose film.

Pressure with and Without Surface Abrasion

Five levels of pressure during bond drying and four degrees of abrasion were investigated to determine effects of pressure and abrasion on cellophane adhesion. The experimental data are presented in Table XIV and depicted in Fig. 9. Table XV summarizes the results. The procedures used have been described previously. The following observations are pertinent:

1. Adhesion was a strong function of both the degree of substrate abrasion and the level of the pressure maintained during drying. A combination of surface abrasion and pressure during bond formation was capable of giving high adhesion levels of ca. 185 kg./cm.^{2}, i.e., double that of the control specimens.

TABLE XIV

EFFECT OF ABRASION AND DRYING UNDER PRESSURE ON CELLOPHANE ADHESION FROM WATER[a]

Pressure During Drying, p.s.i.	Degree of Surface Abrasion[b]: None	Mild (30 Strokes)	Moderate (260 Strokes)	Severe (875 Strokes)
	Effective Adhesion, kg./cm.^{2}			
0	91.5	120.9	138.8	147.9
180	113.1	146.9	162.2	159.0
1000	119.0	168.0	174.2	174.2
1900	120.6	166.9	185.8	187.8
2500	121.2	165.1	182.8	189.0
3900	(93.0)[c]	--	--	--

[a] All sheets of cellophane were PUD-0 type and were solvent cleansed by the standard sequence after roughening.

[b] Abrasion was with 303 emery powder by standard procedure.

[c] Damaged due to embossing of cellophane by metal backing plate and by filter papers through three layers of membrane filter.

2. Pressures below 1000 p.s.i. were the most effective in increasing adhesion. Very little improvement in bond strength was achieved by increasing pressures from 1000 to 2500 p.s.i.

3. Mild abrasion resulted in the greatest relative increase in adhesion as compared to nonabraded cellophane. Moderate roughening gave a small increase in bonding over that attained as a result of mild abrasion. However, severe roughening did not significantly increase adhesion of cellophane over that obtained through moderate roughening.

4. Effective adhesion was raised 32% by the use of pressure alone, 62% by abrasion alone, and 107% by a combination of abrasion and pressure. Thus, abrasion appears about twice as effective as pressure and the combination of pressure and

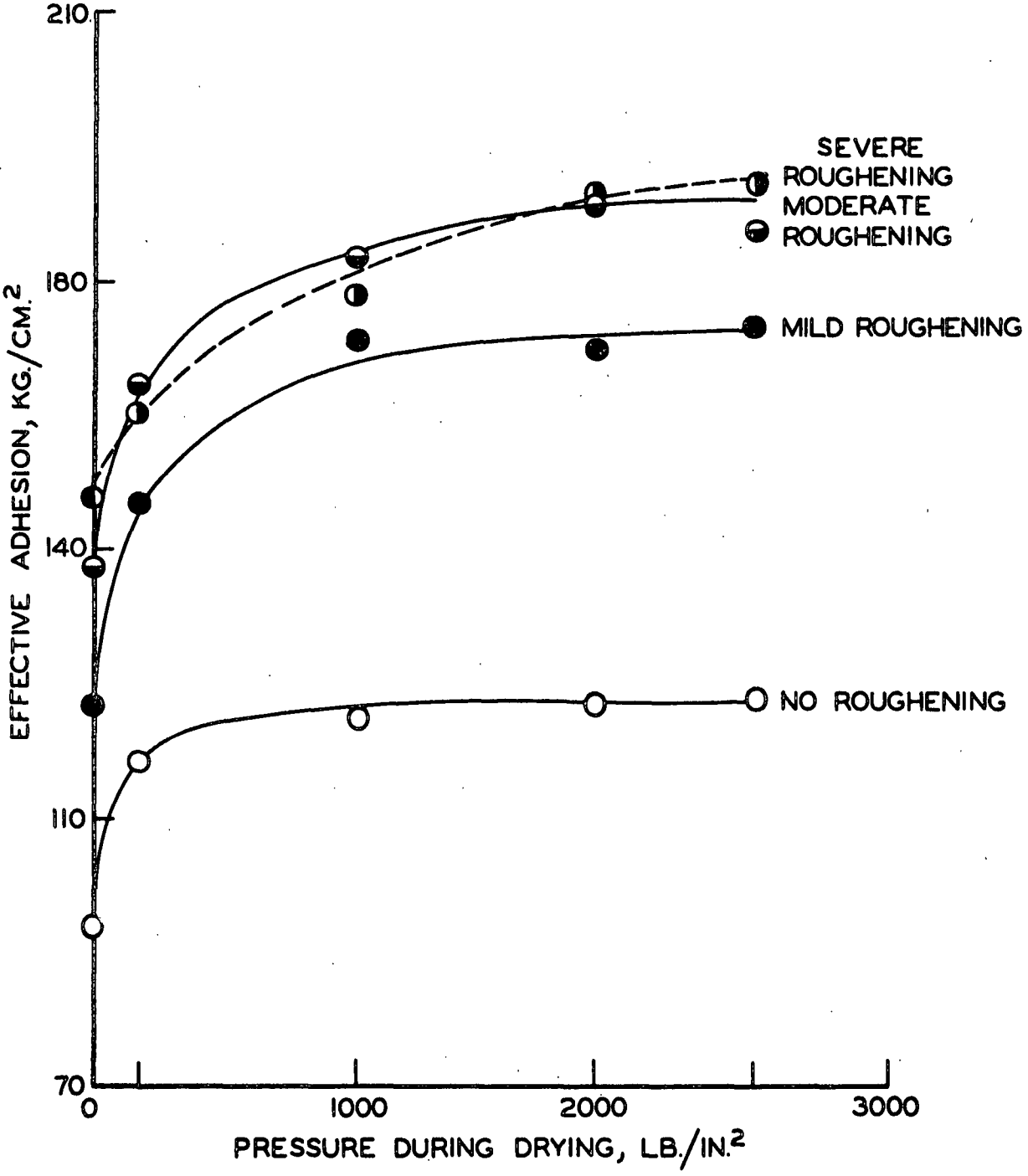


Figure 9. Effect of Abrasion and Drying Under Pressure on Cellophane Adhesion from Water

abrasion has an essentially additive effect on the effective adhesion between cellophane films bonded from water.

TABLE XV

COMPARISON OF EFFECTS OF ABRASION AND PRESSURE DURING DRYING ON CELLOPHANE ADHESION FROM WATER[a]

Optimum Abrasion	Optimum Pressure	Effective Adhesion, kg./cm.^{2}	Increase in Adhesion Due to Treatment(s), %[b]
No	No	91.5	--
No	Yes	121.2	32
Yes	No	147.9	62
Yes	Yes	189.0	107

[a] Data obtained from Table XIV.

[b] The percent increase is calculated using the effective adhesion value of the specimens having no abrasion and no pressure during drying, i.e., 91.5 kg./cm.^{2}.

These results are evidence that the adhesion of cellophane to cellophane is very dependent upon the degree of molecular or near-molecular contact between the two surfaces. The possible reasons for increase in interfacial contact are:

A. The surfaces approached "smoothness" on a molecular level.

B. The surfaces were capable of flowing viscoelastically upon contact during bond formation.

C. The surface area available for molecular contact was increased as a result of surface abrasion and plasticization by water.

D. An intermediary material was present to "bridge-the-gaps" between the surfaces.

Consideration (A), above, is not tenable for this system because cellophane, although very smooth for a solid surface, has finite surface irregularities in the order of 500 to 1500 A. (see Table XI).

External pressure applied during bond formation would greatly increase the viscoelastic flow of the cellophane films (Factor [B] above). Figure 9 showed that initial increments of increased external pressure (i.e., those below 1000 p.s.i.) were more effective in increasing adhesion than later and higher pressure increments. Three reasons for this may be given:

1. The initial low levels of pressure application could cause the two cellophane surfaces to be moved and held closer to each other during drying so that surface tension forces could develop very high localized pressures (e.g., 4000 p.s.i. at 50 A. separation) to force the surfaces to within a few angstroms where intermolecular forces would become effective.

2. The gross positioning mechanism of (1), above, requires relatively low external pressure to be effective in comparison to flow deformation of the solids. Surface flow deformation would increase markedly the cellophane contact area supporting the external load, so that the amount of external load needed to cause flow of the remaining asperities would increase. The most prominent "hills" of the two surfaces would be "flattened" first. Additional external forces would concentrate at these new regions of contact and, unless considerable flow of these already flattened asperities could occur, new areas of interfacial contact would form only with great difficulty. Hence, this would explain the experimentally observed leveling-off of the effectiveness of external pressure in achieving increased adhesion. Consistent with this, Maxey (147) found that the contact area increase of end-grain wood was about three and one-half times more rapid during the initial pressure increments than during the latter increments. Also, the contact area tended to level off at about 60% of the total area at a pressure application of 2000 p.s.i.

3. A possible explanation of the ineffectiveness of high pressures in this study is the development of severe mechanical stress concentrations at the interface. This is illustrated by the experimental observation (Table XIV) of the great loss of effective adhesion when external pressure was raised from 2500 to 3900 p.s.i. Examination of the bonded films showed mechanical damage due to an embossing of the cellophane caused by the metal backing plate and the roughness of the filter paper.

Factor (C) (p. 102) considers the increase in surface area due to abrasion and plasticization. There are several explanations possible for the positive effect of abrasion on adhesion; viz., a more complete cleansing of the surface, chemical modification, increased area of surface-to-surface contact, and increased mechanical interlocking of the surfaces. The results of Table XIII showed that abrasion was not very effective in removing surface contamination. Chemical modification can be ruled out because of the very mild, physical nature of the abrasion process. The increased adhesion with abrasion is explainable on the basis of two hypotheses; viz., (1) the number of available active bonding sites per unit area of cellophane is increased, and (2) the effective "mobility" of the surface is increased through the increased plasticization of the cellulose by water and through the reduced cross-sectional dimensions of the structural elements created on the surfaces.

Abrasion may be considered as the creation and/or liberation of fibrillar structural elements from relatively inactive cellophane surfaces. A number of studies (148-151) present good evidence that the surfaces of cellophane are comprised of dense, thin layers of oriented structural elements. Thus, the structural elements of a dried cellophane surface are believed to be mutually bonded to such an extent that reswelling in water cannot fully activate the surfaces. Therefore, mechanical action such as abrasion appears necessary to free some of the structural

elements and to make them available for bridging the distance to a contiguous cellophane surface, which increases bonded area.

Cellophane is plasticized by water (modulus of elasticity reduced) by the breaking of some of the hydrogen bonds between cellulose chains (152, 153). The projections of the surface of abraded cellophane would be capable of swelling more in water because they would be less restricted by the structure of the bulk film, and also since the ease of flexure of solid elongated structures of circular cross section is inversely proportional to the fourth power of their diameter. Small structures produced by abrasion of cellulose surfaces would be more deformable under pressure and so capable of being drawn into closer contact more readily by capillary pressure. Thus, this greater surface mobility would lead to an increase in the area of intermolecular bonding.

It is not believed that the diffusion theory of autohesion (p. 37) is applicable to the cellophane-water-cellophane system. The diffusion theory appears to require more actual mobility on a molecular level than can be present on the surface of cellophane. It is very improbable that the roughening of a dry cellophane surface with emery would liberate individual molecules (or segments of molecules) which could participate in the necessary molecular transport process. Confirming evidence for this was given by Swanson (154) who found that the storage of wet paper handsheets gave no improvement in cellulose fiber bonding.

This highly restricted surface mobility of cellophane would rule out any significant amounts of mechanical interlocking or wedging as proposed by the adherents of the mechanical adhesion theory (p. 35).

Under normal environmental conditions, it is very probable that cellophane surfaces exist which have regions containing several monolayers of water. Since the existence of hydrogen bonding of water molecules to themselves and to cellulose

is widely accepted, it is postulated that water acts as an "adhesive" between the cellophane films. Thin films of water between solids have been shown to have adhesive properties (79, 155-157) and to possess a theoretical cohesive strength of about 4300 kg./cm.^{2}. Real bonds with water are not expected to approach this theoretical cohesive strength because even strongly sorbed liquids like water have very little resistance to flow along a surface under shear stress. Water which is confined to restricted regions where shear is not possible, would exhibit tensile strength closer to theoretical. Several workers (101, 158-160), using different approaches, calculated works of adhesion, W_A (p. 30), for cellulose-water, and starch film-water at 121-134 ergs./cm.^{2}. Also, the works of cohesion, W_c (p. 30) for cellulose and starch films was reported as 86 to 123 ergs./cm.^{2}, while water has a W_c value of 146 ergs./cm.^{2}. It appears that in the systems cellophane-water-cellophane, cellophane-cellophane and cellophane-starch-water-cellophane, thermodynamics predicts that all systems have strengths of adhesion and cohesion of the same order of magnitude. Actually, based on the above values, water should be the strongest link in the chain of cellulose-water-starch. If we assume that 4×10^{-8} cm. displacement is required to rupture a bond due to hydrogen bonding, the following approximate theoretical forces for failure may be calculated for these systems: water cohesion 3,700 kg./cm.^{2}, cellulose and starch cohesion 2,650 kg./cm.^{2}, and water adhesion to cellulose or starch 3,190 kg./cm.^{2}. These theoretical values are, of course, at least 10 times higher than experimental for reasons which were discussed previously (p. 26).

The final factor ([D], page 102) which should be discussed as a possible reason for increase in interfacial contact in this study is that of the presence of an intermediary material, i.e., an "adhesive." The above experiments employed water as the "adhesive" and it proved to be partially effective. We must say partially because less than 20% cohesive failure of the cellulose film occurred

during bond failure, even though high bonding pressure and surface abrasion were utilized to achieve maximum interfacial contact. It must be concluded that water is not a totally effective adhesive. Its small molecular size and lack of resistance to shear stress does not provide much potential for gap-bridging between cellulose surfaces which are far from being molecularly smooth. Larger molecules are needed for spanning the adherend surfaces.

STARCH FILM THICKNESS IN CELLOPHANE ADHESION

CELLOPHANE ADHESION WITH WHOLE AMYLOSE AND AMYLOPECTIN

Water, abrasion, and pressure were only partially successful in achieving good interfacial contact as indicated by measurements of effective adhesion. This section describes experiments using aqueous solutions of pure amylose and amylopectin of high molecular weight (1.1×10^6 and 4.8×10^6, respectively).

All of the cellophane-amylose-cellophane bonds prepared using the sorption technique (Table III) were evaluated and, with the exception of Code 31-D, gave adhesion strengths which were statistically identical to the controls using water. Bond assembly 31-D gave effective adhesion of 109 kg./cm.^{2}, or 21% higher than the control. Quantitative measurement of the amount of starch in the bond yielded only 0.01 to 0.02 g./m.^{2}. This amount of starch was found (see below) to be about 10% of that necessary to attain maximum adhesion.

Table XVI and Fig. 10 summarize the adhesion results obtained using the evaporation technique and various amounts of molecularly dispersed, aqueous amylose and amylopectin. A large proportion of the initial results are not included in Table XVI because they involved (1) a lack of preabrasion of external surfaces of the cellophane and/or (2) open assembly times in excess of three minutes, both of which contributed to low effective adhesion.

TABLE XVI

SUMMARY OF CELLOPHANE ADHESION AS A FUNCTION OF AMOUNT OF STARCH IN BOND

Code	Amt. of Starch, g./m.^{2}	Thickness of Starch, A.[a]	Effective Adhesion,[b] kg./cm.^{2}	Cohesive Failure of Cellophane, %	Nature of Failure
Amylopectin, Whole Fraction					
Control	0	0	92.8	1	Scattered
3-23-JA	0.0037	25	112	5	Scattered
3-23-E	0.0074	50	132	12	Scattered
3-23-FB	0.0148	99	177	20	Scattered
	0.050	340	227	24	Scattered
121-A	0.13	870	231	21	Scattered
121-B	0.32	2,100	308	36	Scattered
121-C	0.65	4,400	312	35	Scattered
121-D	1.14	7,600	303	34	Scattered
121-E	1.62	10,900	310	51	Scattered
121-F	2.27	15,200	307	39	Scattered
121-G	8.75	58,700	279	31	Scattered
G-89	63.60	427,000	202	23	Peel, partial
Amylose, Whole Fraction					
47-2203-A	0.019	130	143	25	Scattered
0-9-1C	0.037	250	155	21	Scattered
32-C	0.047	320	180	32	Scattered
47-2203-B	0.071	480	257	37	Scattered
47-2203-C	0.14	940	282	42	Scattered
47-2203-D	0.41	2,800	294	60	Scattered
47-2203-E	0.81	5,400	300	51	Scattered
47-2203-F	2.17	14,600	238	20	Peel
47-2203-G	4.33	29,100	220	18	Peel
47-2203-H	10.17	68,200	222	20	Peel

[a] Calculated from the experimentally determined density of the starch films, 1.49 g./cc.

[b] Mean of five to ten determinations. Coefficient of variation ([Standard Deviation/mean] x 100) is 10% or less.

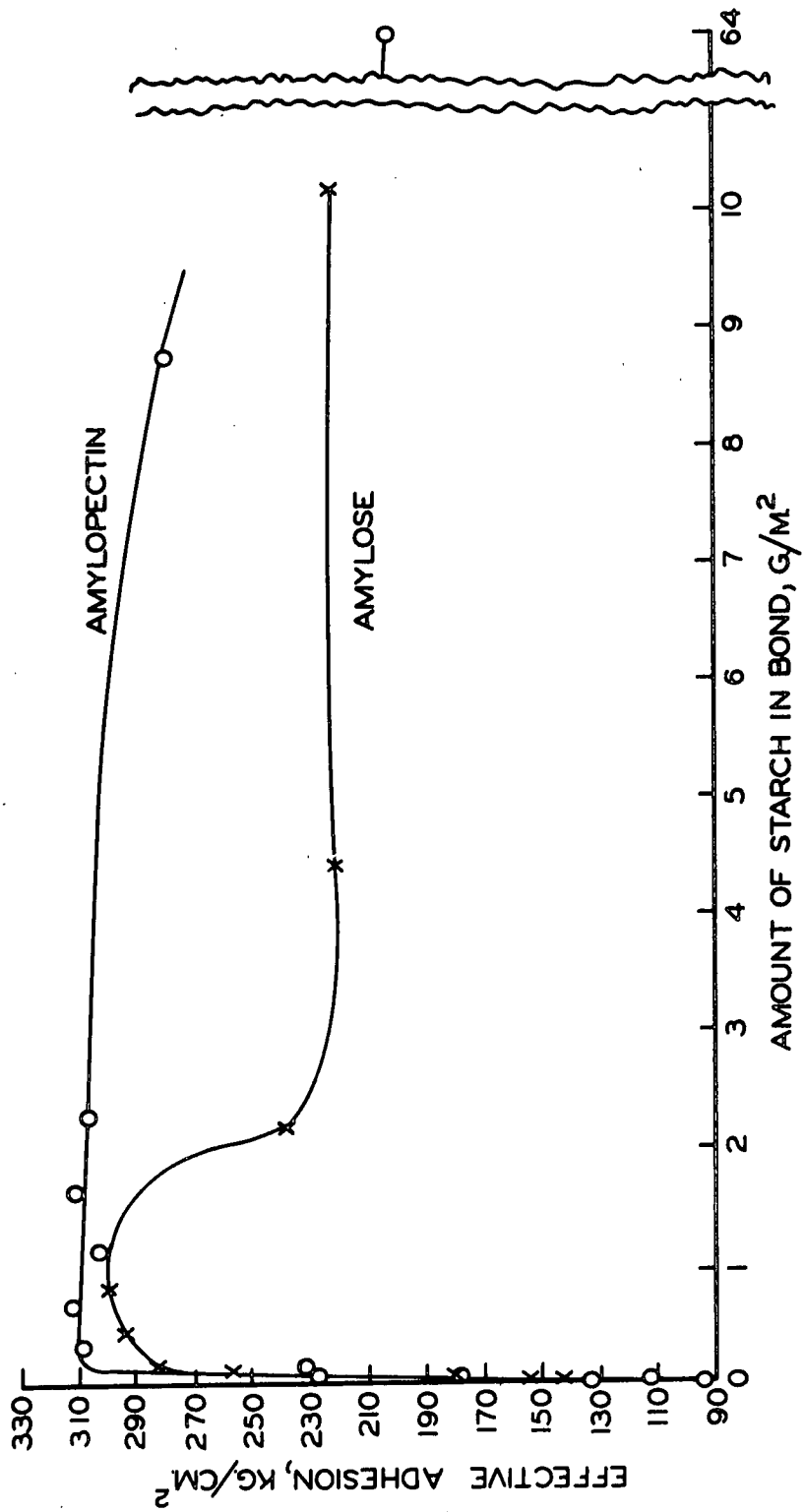


Figure 10. Cellophane Adhesion as a Function of Amount of Starch in Bond

Figure 11 is a photograph showing the top view of one test surface after failure of a cellophane-amylopectin-cellophane bond where the external cellophane surfaces were not preabraded. The amylopectin is evident from the dark regions created by staining with iodine solution. The undesired peel failure of the cellophane-epoxy bond is visible at the lower one-quarter of the specimen area where the cellophane peeled during testing from the epoxy adhesive of the other cylinder of the test pair. Peel failure such as this resulted in as much as an 80% decrease in test values. No peel failure of cellophane-epoxy bond was evident in any specimens when external preabrasion of the cellophane was used with open assembly times less than two minutes.

Figure 11. Photograph of a Cellophane-Amylopectin-Cellophane Failure Zone. Peel-Type Failure of Cellophane-Epoxy Bond Evident at Bottom Quarter of Zone. Enlargement: 3X

The following results of Table XVI and Fig. 10 are significant:

1. There was an extremely rapid increase in effective adhesion as very small amounts of amylose and amylopectin were used.

2. A relatively sharp maximum adhesion was reached with very small amounts of either amylose or amylopectin in the bond. This adhesion maximum remained at a broad plateau for amylopectin and a narrow plateau for amylose as adhesive film thickness was increased. These effective adhesion maxima and plateaus were reached with 0.10 to 0.20 g./m.^{2} (670 to 1340 A. equivalent thickness) of starch between the cellophane films.

3. Amylopectin and amylose were very comparable in the maximum effective adhesion attained, viz., 310 and 300 kg./cm.^{2}, respectively. However, amylose was much more sensitive than amylopectin to increase in film thickness. Increasing the amylose beyond about 1.0 to 2.0 g./m.^{2} resulted in a sharp, 25% decrease in effective adhesion to a lower plateau of about 220 kg./cm.^{2}.

4. Increasing the adhesive film thickness of amylopectin caused a very gradual decrease in effective adhesion of cellophane until, for very thick bonds of over 60 g./m.^{2} (43 μm. equivalent thickness), adhesion was 35% below the maximum, plateau level.

Adhesive Film Thickness and Surface Irregularities

This section makes conclusions based on the above results and the surface configuration of the cellophane. The very rapid rise in effective adhesion with small increased amounts of starch adhesive may be attributed to the achievement of increased "bridging" contact between the cellophane adherends by the starch molecules. This conclusion is substantiated by consideration of the size of the surface irregularities of the adherend and the thickness of the starch film

required to achieve maximum adhesion. The Brush analysis of the size of surface irregularities of the cellophane film (Table XI) indicated that the average imperfection was about 750 A. above and below the reference plane of the surface. Doubling of this value to account for both films which comprise the bond gives 1500 A., which corresponds in order of magnitude to the nominal starch film thickness required to attain maximum adhesion (670 to 1340 A.).

Another calculation to approximate the void volume between two cellophane films may also be made. If we choose a basis of one square meter of cellophane film, the total volume of the rectangular parallelpiped which includes the average height of surface imperfections is equal to 1.5×10^{23} A.^{3} (1×10^{10} A.^{2} x 1500 A.). As an approximation it may be assumed that the shape of the imperfections is rectangular along both the length and width directions of the film. Then, the volume of the irregularities is equal to one-fourth (1/2 x 1/2) of the total volume of the parallelpiped, or 0.375×10^{23} A.^{3}. Since the volume occupied by one gram of starch is 0.672 cc. (1.00 g./1.49 g./cc.), the weight of starch to just fill in the voids between two films is approximately 0.33 g./m.^{2} (2.25×10^{23} A.^{3}/1 x 10^{24} A.^{3}/cc. x 0.672 cc./g.). The check between this value and the 0.1 to 0.2 g./in.^{2} of starch required experimentally (Fig. 10) is satisfactory considering the approximations and assumptions involved in the calculation of the void volume between the films.

Thus, the experimental fact that the optimum adhesive strength is attained with just sufficient adhesive to "fill in" the voids between the films, substantiates the hypothesis that the primary function of an adhesive in this system is to establish maximum "bridging" of the voids between the solid adherends.

As the adhesive film thickness increases beyond the optimum, the adhesive merely served to separate the cellophane surfaces with thicker and thicker films of starch. Amylose-cellophane bonds were much more sensitive to adhesive film

thickness than amylopectin-cellophane bonds. In the case of amylose a very rapid decrease in adhesion with adhesive film thickness occurred. With amylopectin, there was only a very gradual decrease in effective adhesion of cellophane as the amount of amylopectin was increased (Fig. 10). No change in the nature of bond failure was observed with increasing film thickness except in the set of thickest bonds (63.6 g./m.^{2}) which exhibited a tendency toward "peel" failure of the amylopectin. "Peel" failure refers to bond rupture such that almost all of the starch is found on one of the cellulose surfaces, i.e., the starch appears to have "peeled" from one surface (Fig. 12). In contrast, normal failure results in starch distributed in a "shatter" pattern on both adherends (Fig. 13).

Internal stress concentrations formed during bond formation and testing are increased with adhesive film thickness (74, 120). However, it may be concluded that the theory of occurrence of more flaws as the thickness of a bond increases is not applicable because in that case the location of the plane of failure would be random in the adhesive. Failure in our experiments was at the interface, especially evident for the relatively thick bonds.

Cohesive Failure of Cellophane Adherend and Nature of Failure Zones

As the effective adhesion of the cellophane-starch-cellophane bonds increased, so did the degree of internal cohesive failure of the cellophane. This relationship is graphed in Fig. 14 where it may be noted that the extent of cellophane failure ranged from about 1 to 60% of the geometric area of the bond as the level of effective adhesion increased from 93 to 321 kg./cm.^{2}. Since effective adhesion was directly related to the extent of cellophane failure (Fig. 14), one may conclude that failure was determined by factors other than the cohesive strength of the cellophane. In other words, if the cohesive strength of cellophane was the weak-link in the bond, effective adhesion would not exhibit the increase shown once any cellophane failure occurred.

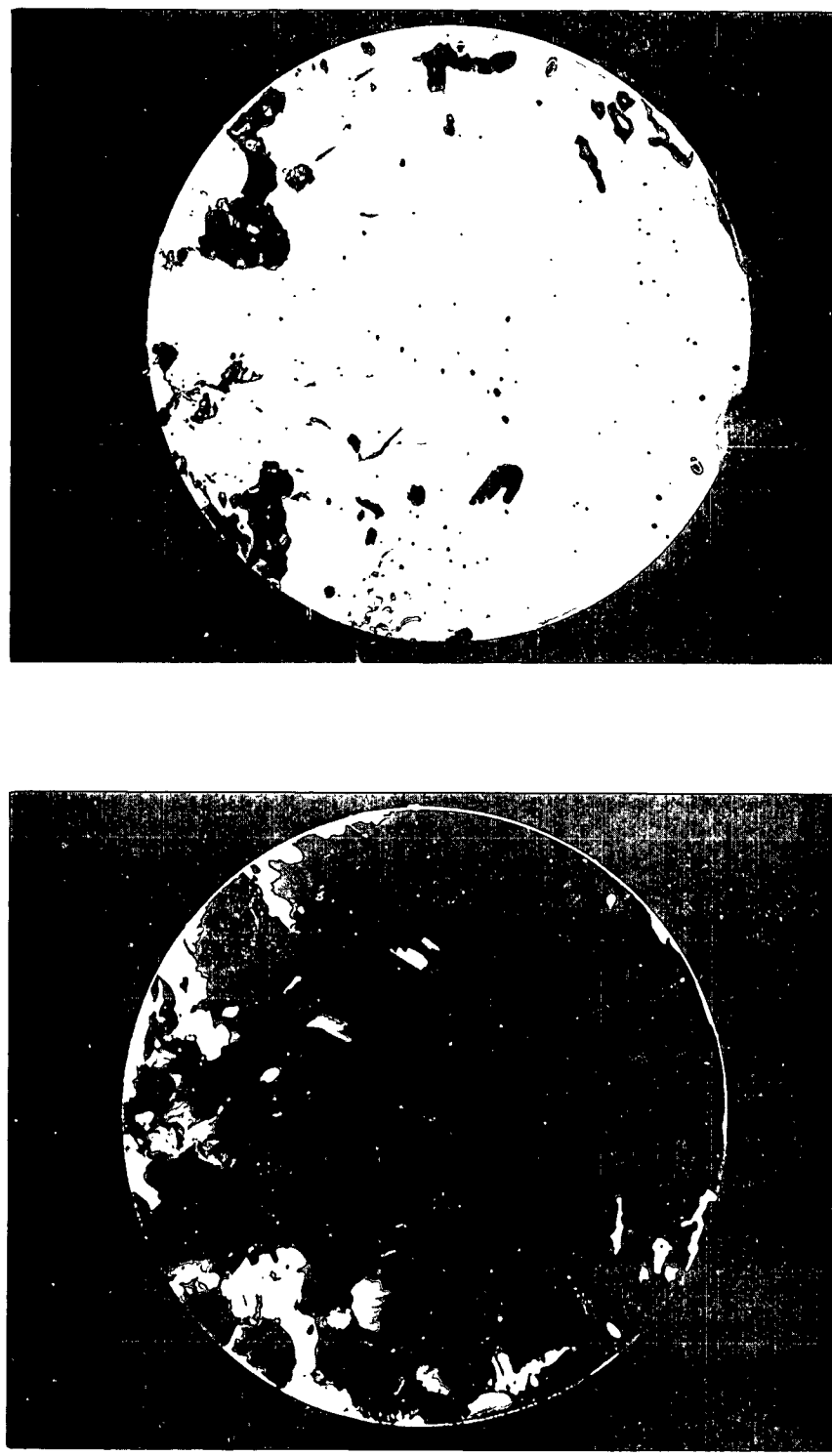


Figure 12. Amylose-Cellophane Bond Failure Zone Showing Peel Pattern Effective Adhesion: 200 kg./cm.^{2}. Adhesive Quantity 2.17 g./m.^{2}

Figure 13. Top View of the Two Failure Zones After Rupture of a Typical Cellophane-Amylopectin-Cellophane Bond Assembly. Magnification: 3X

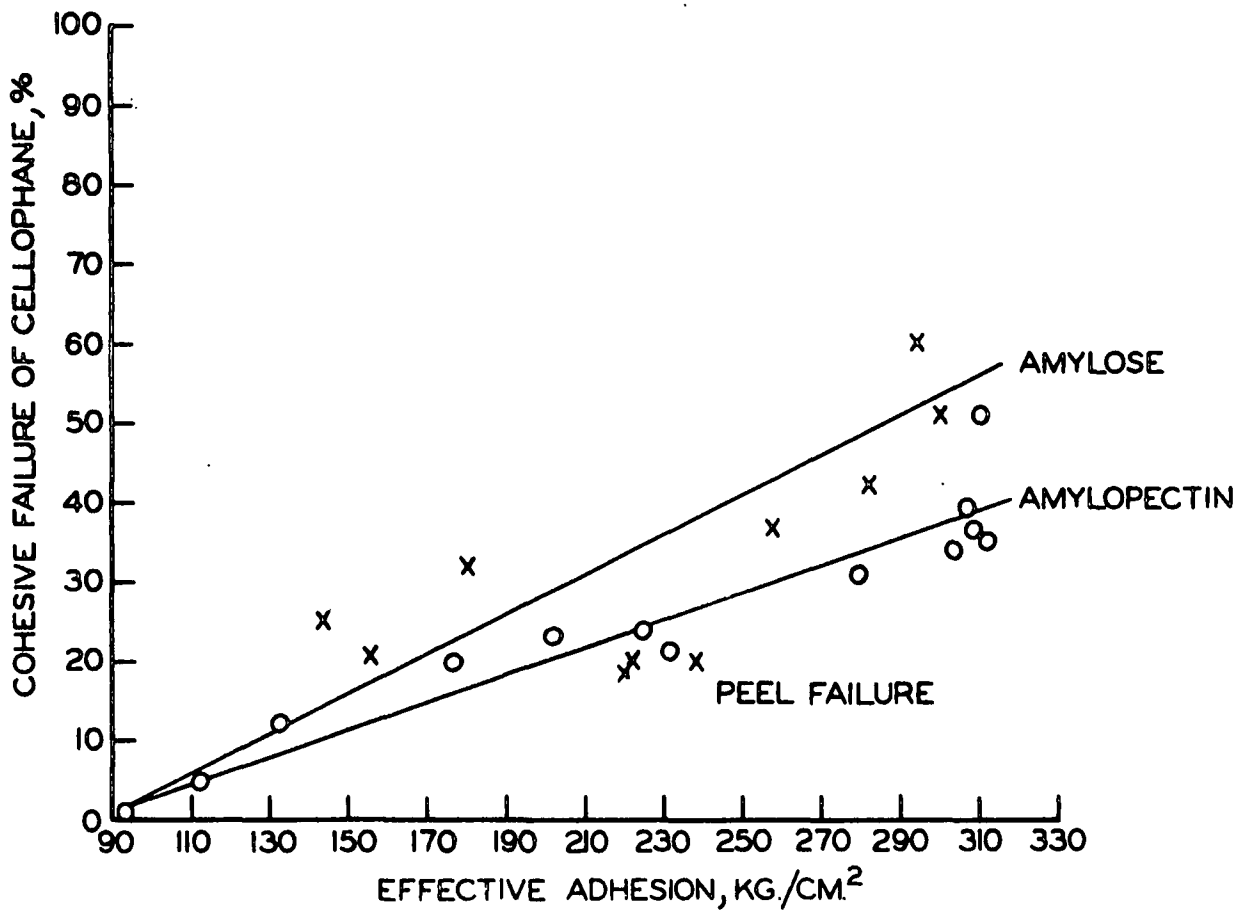


Figure 14. Effect of Adhesion on Extent of Cohesive Failure of Cellophane

Because of the mixed, heterogeneous nature of the rupture zones (e.g., Fig. 13) it is difficult to ascertain where failure started. Judging from the directional "burst" pattern of the fracture lines, fracture started at a region above and to the left of center of the top picture. There does not appear to be any cohesive failure of the amylopectin, since the matching nature of the fracture lines indicates mixed adhesive failure (mixed amylopectin-to-cellulose failure). This does not rule out the possibility that the amylopectin failed cohesively (internally) first and that the zone of failure then transferred to an adhesive type between the amylopectin and the cellulose.

It appears that as the effective adhesion of the cellophane-to-starch joint increases, an increasing proportion of the bonded zone becomes sufficiently strong enough to cause cellophane failure.

Cellophane-Amylose Bonds and Peel Failure

Peel-type failure was much more prevalent in amylose bonds, even at very low adhesive film thicknesses, than in amylopectin bonds. Typical peel-failure of amylose bonds was illustrated in Fig. 12, whereas the appearance of amylose scattered failure zones was the same as shown in Fig. 13. Extensive cohesive rupture of the cellophane surfaces occurred with the strong, scattered type failures, whereas in peel-failure only limited, shallow cellophane failure was noted, about 90% of the amylose remained on one adherend, and adhesion level was low.

Referring again to Fig. 14, the three sets of amylose-cellophane bonds having adhesive thicknesses beyond the 1.0 g./m.^{2} plateau high-adhesion range are indicated, and may be observed to have cohesive cellophane failure levels much below those exhibited by the thinner amylose bonds at a given effective adhesion. It is evident, therefore, that the nature of failure of the thick amylose-cellophane

bonds was different from those below the critical film thickness. Amylose was much more sensitive to film thickness variations than was amylopectin. This difference has to be attributed to factors other than surface energies since these are similar for both types of starch. Furthermore, the thickness of a starch film would not affect surface energies.

Effective Adhesion and Mechanical Properties of Starch and Cellophane

Tables XVII and XVIII present data comparing the mechanical properties of the adhesives and adherends with the experimentally determined maximum bond assembly strength values. Evaluation of the Z-direction cohesive strength of the films was obtained after abrasion of the surfaces. This was necessary in order to avoid gross failure of the epoxy-film bond. Figure 15 illustrates the total cohesive rupture of a single cellophane film when originally bonded between the test cylinders and tested to failure.

TABLE XVII

MECHANICAL PROPERTIES OF CELLOPHANE AND STARCHES

	Tensile Ultimate, kg./cm.^{2}	Elongation to Break, %[a]	Elastic Modulus, kg./cm.^{2} x 10^{-4}[b]	Elastic Limit, kg./cm.^{2}[c]	Cohesive Strength, (Z-Direction Tensile), kg./cm.^{2}	Adhesion Plateau, kg./cm.^{2}[d]
Cellophane						
MD	970	7.8	10.70	497	322	--
CD	1580	17.7	6.89	310	--	--
Amylopectin, whole	475	3.5	2.88	149	236	310
Amylose, whole	533	13.9	3.12	157	191	300

[a] Percent based on initial span.
[b] Based on slope of stress vs. strain curve.
[c] Point on stress vs. strain curve where deviation from linearity occurred.
[d] See Fig. 10.

TABLE XVIII

COMPARISON OF ADHESION AND STRENGTHS OF CELLOPHANE, AMYLOSE, AND AMYLOPECTIN[a]

	Strength Ratios				
	Adhesion/ Starch-XY	Adhesion/ Starch-Z	Adhesion/ Cellophane-Z	Starch XY/ Cellophane XY[b]	Starch-Z/ Cellophane-Z
Amylopectin	0.65	1.31	0.96	0.37	0.73
Amylose	0.56	1.57	0.93	0.42	0.59

[a]

[b]Based on the strength data of Tables XVI and XVII (p. 108 and 118).
Cellophane XY value used was mean of MD and CD direction.

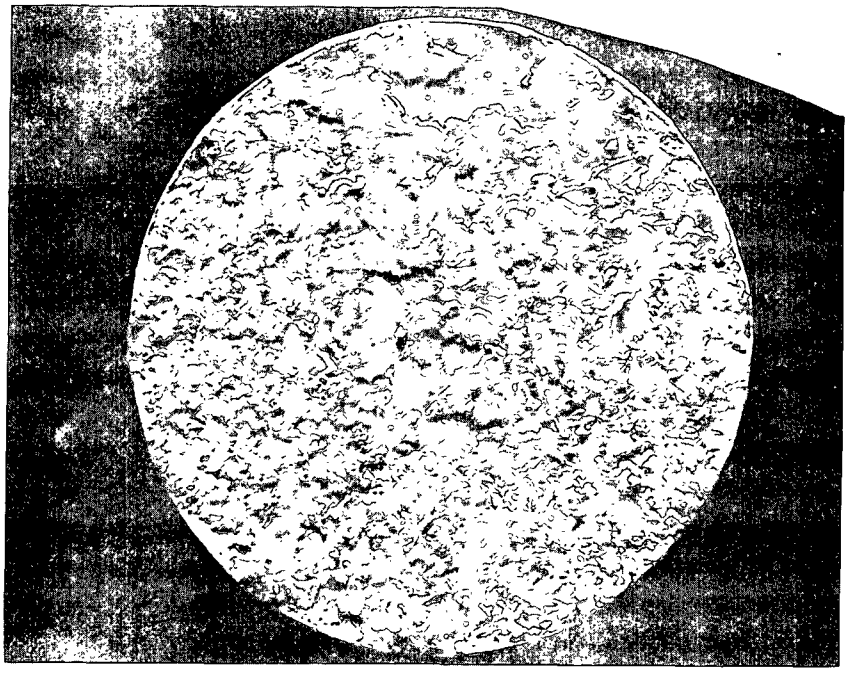


Figure 15. Cohesive Cellophane Rupture Surface After Z-Direction Testing
Magnification: 3X

It is evident from Table XVII that the Z-direction cohesive strengths of the amylose, amylopectin, and cellulose films gave a more reliable estimate of effective adhesion of the bonds than did the corresponding in-plane, XY-tensile strengths.

Table XVIII compares the maximum effective adhesion of cellophane obtained with amylose and amylopectin with the XY- and Z-strength of the amylose, amylopectin, and cellophane. The magnitude of maximum adhesion closely corresponded to the Z-direction cohesive strength of the cellophane, i.e., a 0.96 and 0.93 to 1.00 ratio for amylopectin and amylose, respectively. The XY-direction strength of the cellophane films was much beyond the observed adhesive strengths of the bonds and would, therefore, not account for the high degree of cohesive cellophane failure found during bond testing. The Z-direction test, on the other hand, showed that the cellophane was three to five times weaker in the Z-direction than in the XY-plane. Z-direction tensile tests yielded a cohesive strength virtually equal to the highest effective adhesion found in the cellophane-starch-cellophane bonds. On this basis, the high degree of cellophane failure during the fracture of the adhesive joints becomes understandable.

The cohesive strengths of the amylopectin and amylose films as evaluated by the Z-direction technique were only about two-thirds that of both the cellophane strength and the optimum effective adhesion of the bonds. However, the XY-direction tensile strengths of both amylose and amylopectin were ca. 40% greater than the maximum effective adhesion values of the bonds. Z-direction tensile strength measurements could be on the low side for several reasons, which would improve the correspondence of Z-tensile of the starches and their adhesion performance. The possible reasons are:

1. The starch films had to be abraded in order to achieve satisfactory adhesion to the epoxy adhesive used for attaching the specimens to the metal, test

cylinders. This abrasion could cause mechanical damage to the starch films and introduce stress concentrations. The starch films present between the cellophane films are not subject to this.

2. The films tested were much thicker than those present in the adhesive bonds of maximum strength. Based on the weak-link theory (96, 97) the less material in the specimen, the lower the probability of the occurrence of flaws of a given severity and, therefore, the higher the mean strength of the material. If the flaws are assumed to be distributed randomly throughout the adhesive, bond failure would be initiated in random locations within the adhesive or at the adhesive-adherend interface. However, if flaws concentrated at the interface because of crystallization, incompatibility, incomplete wetting, etc., then failure along the adhesive-adherend interface would be favored.

3. Greater probability existed for stress concentration (and, thus, lower strength) when the epoxy was bonded directly to the starch film, than when the starch film was protected from uneven stressing by the buffering and cushioning action of the cellophane films on either side of the starch film.

Application of the weak-link theory to the XY-direction strengths of the starch or cellophane films would increase the strength values so that the discrepancy between adhesive bond strength and XY-strength would be even greater. Thus, it may be concluded that both cellophane and starch film strength in the Z-direction correlated much better with adhesion behavior than did the conventional XY-directions strength tests.

There was only a small difference in the strength of amylose and amylopectin films, both in the XY- or Z-direction as indicated in Table XVII. Amylose had slightly higher XY-tensile strength, whereas amylopectin had slightly greater Z-direction strength, The largest difference in the mechanical properties of the

two films was in their extensibility in the XY-direction, amylose exhibiting four times greater elongation before failure than amylopectin. Based on XY-direction strength and elongation one would expect amylose to be a better adhesive than amylopectin. Such was not the case since amylopectin showed superior adhesion over a much wider range of adhesive film thicknesses than did amylose. Again, the Z-direction strength predicted a slight superiority of amylopectin as an adhesive.

The causes for the differences in strength properties in the two test directions should be mentioned. The films used in this study were not homogeneous in molecular or crystallite orientation. Cellophane has a layered structure with orientation of its fibrillar elements essentially parallel to the plane of its surface. On this basis, one would expect lower strength when stress is applied perpendicular to the surface (as is the case in butt-adhesive bonds of this study) than when the tensile strength of the films is evaluated in the plane of the film. Starch films formed by evaporation on flat surfaces would also be expected to be anisotropic with respect to the planer (XY) and thickness (Z) directions. Sheppard and McNally (160) proved this to be the case with gelatin films formed by evaporation.

MOLECULAR PROPERTIES OF AMYLOPECTIN AND AMYLOSE AND THEIR EFFECT ON ADHESION OF CELLOPHANE

INTRODUCTION

The previous sections dealt with the adhesion of cellulose films as accomplished through the use of water, whole amylose, and whole amylopectin as adhesives. The factors considered in this section are molecular branching, molecular weight and dimensions, molecular aggregation, and diffusion.

MOLECULAR PROPERTIES OF STARCH FRACTIONS

Molecular Weight and Dimensions

Light-scattering measurements of molecular weight and dimensions were made on all amylose and amylopectin fractions used in this study. Appendix IX gives the data and concentration-turbidity plots. Table XIX gives a summary of the data on molecular weight and size of the amylopectin and amylose fractions. The molecular weight of eight amylopectin fractions ranged from about 4.8 million to 17,000, and of four amylose fractions from 1.1 million to 70,000. A number of fractions were prepared by gel filtration (Table II).

Viscosity data of amylose in water and alkali are presented in Appendix X.

For the aqueous amylose solutions, the very low limiting viscosity values and low slopes of the light scattering (Hc/τ) vs. c plots (Appendix IX) indicated that water was a thermodynamically "poor" solvent for amylose and, thus, amylose molecules were not very extended in aqueous solution. This confirms the work of Cowie (138) and Everett and Foster (139).

Stability of Amylose Solutions

Amylose solutions in water generally are unstable unless very dilute or maintained at high temperature. It was therefore necessary to determine the length of time the solutions could be used in sorption studies or stored before they changed due to molecular association ("retrogradation").

Figure 16 presents the results of aging aqueous amylose solutions of several concentrations at room temperature (23 $\pm$ 2°C.). An apparent molecular weight was calculated from the turbidity ratio, (Hc/τ), and the $P(\theta)$ particle scattering factor, assuming a random coil molecular configuration. The data are tabulated in Appendix XI. It was evident that the length of time during which an amylose solution

TABLE XIX

MOLECULAR PROPERTIES OF STARCH FRACTIONS

Starch Fraction	Molecular Weight, M_w x 10^{-3}	DP_w	Intrinsic Dissymmetry [Z]	Diameter, A.[a]	End-to-End Separation, A.[b]	Limiting Viscosity No.
Amylopectin						
Whole, Amp 121	4780	29,500	1.86	1080	--	--
DF-5, Excluded	511	3,150	1.26	656	--	--
DF-6-SII, Excluded	280	1,730	1.12	459	--	--
DF-5-L	241	1,490	1.04	256	--	--
DF-6	182	1,120	1.03	226	--	--
DF-6-SIII, Included	136	840	--	--	--	--
DF-5-VL	39	240	--	--	--	--
DF-5-IH	17	105	--	--	--	--
Amylose						
Whole - A	1120	6,910	2.01	--	1210	0.47[c] 1.13[d]
Hydrolyzed 0.5 hr.	430	2,660	1.52	--	820	--
Hydrolyzed 1.0 hr.	252	1,560	1.34	--	655	--
Hydrolyzed 3.0 hr.	70	432	--	--	--	--

[a]

[b]Assuming spherical molecular configuration.

[c]Assuming polydisperse coil configuration.

[d]In water at 25°C.

In 0.61N potassium hydroxide at 25°C.

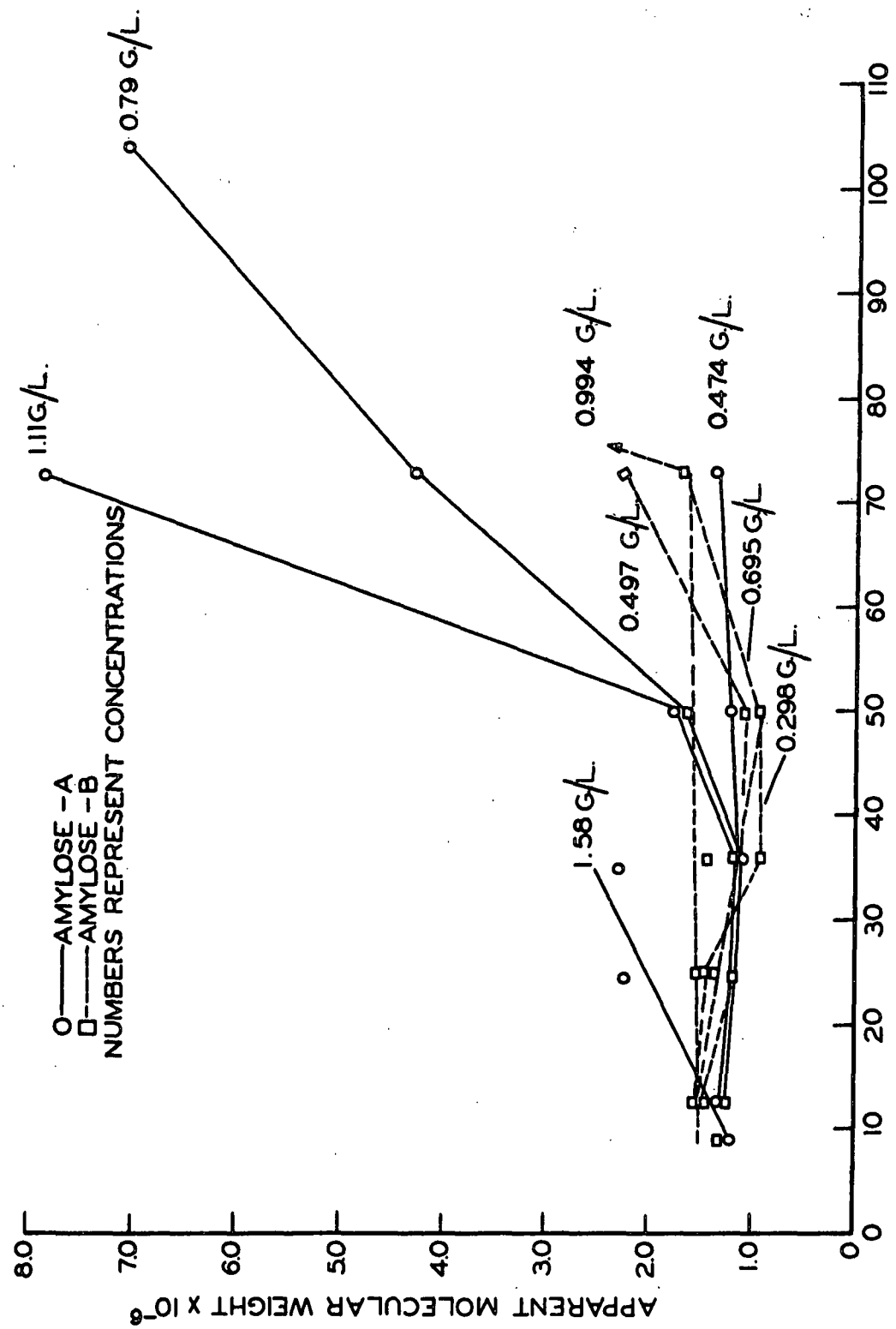


Figure 16. Changes in Apparent Molecular Weight with Aging of Amylose in Neutral Aqueous Solution

was stable was inversely proportional to concentration. Below a concentration of 0.5 g./l., amylose solutions were relatively stable for 70 hours. At about 1.0 g./l. some aggregation of the lower molecular weight amylose commenced after 40 hours. The higher molecular weight amylose appeared to be more stable, requiring over 70 hours for a 1.0 g./l. solution to show marked retrogradation. At concentrations of over 1.6 g./l., instability became apparent between 10 and 20 hours of aging. Thus, for room temperature storage, amylose solutions should be kept below a concentration of 1 g./l., and preferably lower.

MOLECULAR WEIGHT OF STARCH RELATED TO ADHESION AND COHESION

The purpose of these experiments was to determine at what point the mechanical properties of the adhesive film became the limiting factor in the strength of cellophane-starch-cellophane bonds. The previous section showed that the Z-direction cohesive strengths of the adhesive and cellophane films were roughly comparable, i.e., starch films were about 65% as strong as cellophane. If the mechanical strength of the adhesive films was truly the "weak-link" of the bond then bond strength and mechanical properties of the film should show similar response to a reduction in the molecular weight of the adhesive.

Effect of Amylopectin Molecular Weight

Table XX and Fig. 17 present the adhesion results obtained with eight amylopectin fractions varying in molecular weight from 4.8×10^6 to 17,000. Tables II and XIX summarize the molecular characteristics of the fractions. Each data point represents the mean of from five to twenty determinations. The coefficients of variation ([standard deviation/mean] x 100) generally were about 10%.

Four of the low molecular weight fractions gave effective adhesion strengths comparable or slightly higher than did whole fraction amylopectin. The shape of the adhesion *vs.* amount of amylopectin curves obtained was almost identical;

TABLE XX

CELLOPHANE ADHESION AS A FUNCTION OF VARIOUS AMYLOPECTIN MOLECULAR FRACTIONS AND TOTAL AMOUNT OF AMYLOPECTIN

Amylopectin fraction	Effective Adhesion, kg./cm.^{2} [a]							
	Whole Amp-121	DF-5-Excluded	DF-6-S-II	DF-5-L	DF-6	DF-6-S-III	DF-5-VL	DF-5-I H
Molecular weight, $\underline{M}_w \times 10^{-3}$	4780	511	280	241	182	136	39	17
Amount amylopectin Total, g./m.^{2}								
0.0 (control)	93 (1)	95 (2)	92 (1)	94 (1)	92 (2)	93 (1)	93 (1)	94 (1)
0.05	--	219 (23)	--	137 (10)	125 (7)	--	--	--
0.075	--	310 (47)	--	--	--	--	--	--
0.10	231 (21)	324 (60)	--	--	229 (54)	--	128 (8)	--
0.14	--	--	313 (67)	--	--	140 (16)	--	--
0.20	--	312 (41)	--	294 (44)	--	--	152 (15)	130 (12)
0.30	308 (36)	--	--	--	--	--	--	--
0.60	312 (35)	317 (66)	316 (62)	325 (67)	307 (60)	208 (18)	235 (39)	216 (24)
1.1	303 (34)	--	--	--	--	--	264 (34)	--
1.5	310 (51)	--	314 (50)	320 (57)	309 (61)	284 (29)	--	232 (31)
2.3	307 (39)	--	--	--	--	--	--	--
2.5	--	--	--	321 (64)	--	--	--	--
2.8	--	318 (54)	--	329 (52)	--	--	--	--
3.0	--	312 (40)	--	--	--	--	--	--
3.1	--	--	--	302 (48)	--	--	287 (40)	233 (22)
5.5	--	--	--	--	--	297 (40)	--	228 (20)
7.6	--	301 (44)	--	304 (47)	--	--	324 (44)	242 (24)
8.8	279 (31)	--	282 (57)	--	--	--	--	--
12.6	--	--	--	--	243 (16)	--	--	--

[a] Numbers in parentheses refer to percentage of cellophane surface which was ruptured cohesively.

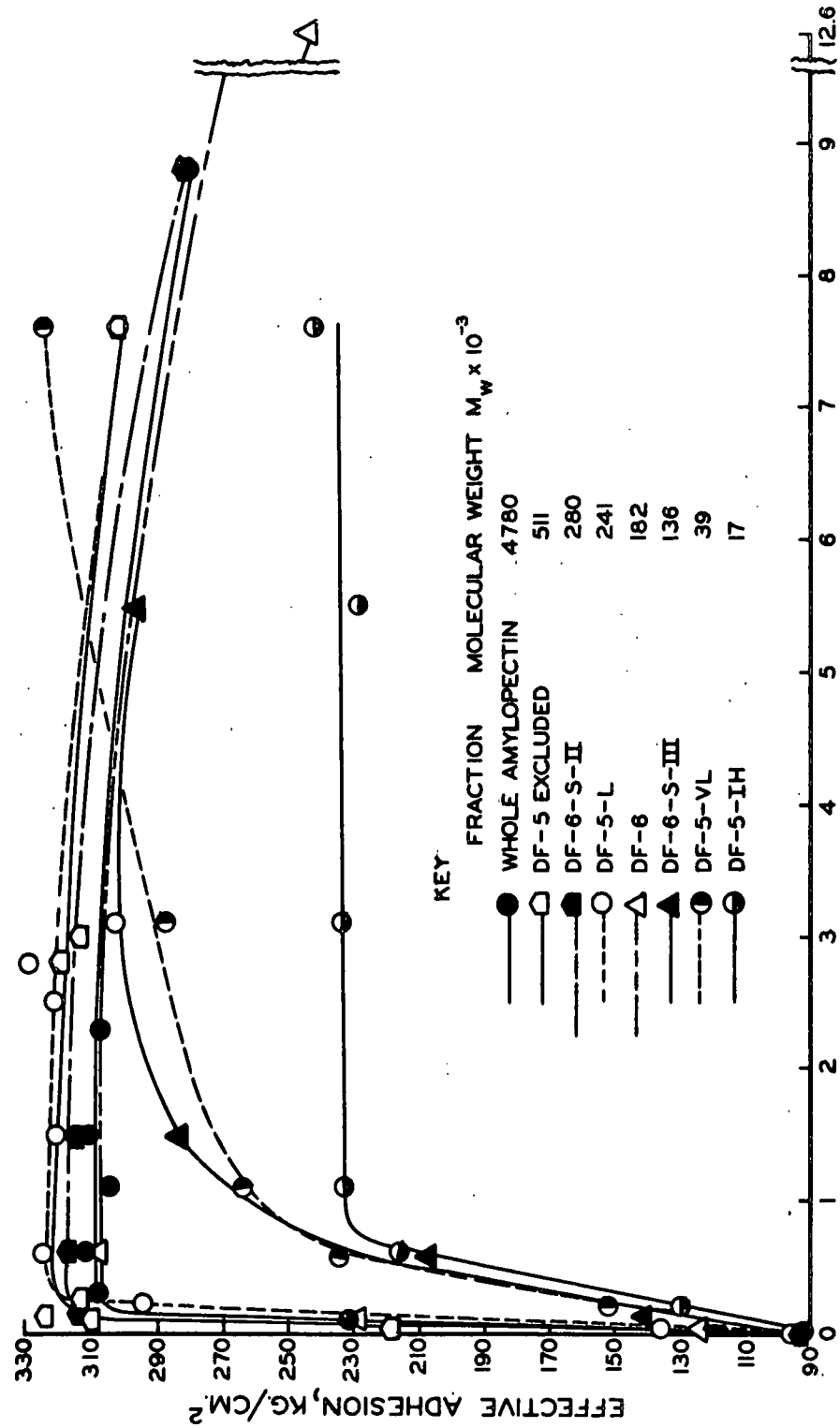


Figure 17. Effective Adhesion of Various Amylopectin Fractions as a Function of Total Amount of Amylopectin

i.e., they exhibited (a) an extremely rapid increase in adhesion with very small initial amounts of amylopectin, (b) a sharp leveling off at about 0.2 g./m.^{2} (1400 A. thickness) of amylopectin, (c) a plateau in effective adhesion between 310 to 325 kg./cm.^{2} attained with starch amounts in the range 0.2 to ca. 3.0 g./m.^{2}, and (d) a relatively slow decrease in adhesion as the amount of starch in the bond increased beyond ca. 3.0 g./m.^{2}. The reasons for the above adhesion response as a function of adhesive film thickness were discussed in the previous section on whole amylopectin.

It is very evident from Fig. 17 that adhesion vs. film thickness for the three lowest molecular weight fractions of amylopectin (136,000, 39,000, and 17,000 $\underline{M}_w$) deviated considerably from the pattern described for the five higher molecular weight fractions. These three amylopectins required much higher film thickness to attain equivalent adhesion levels. This was believed to be due largely to the loss of adhesive from between the cellophane substrates as a result of amylopectin diffusion into the substrate. Of all the fractions studied, only the one of lowest molecular weight (DF-5-IH, 17,000 $\underline{M}_w$) showed markedly lower maximum adhesion than the 300 to 325 kg./m.^{2} level attained by the other fractions. It may be concluded that maximum adhesion in this system is insensitive to molecular weight of the adhesive unless extremely low molecular weights are used.

To test the hypothesis that the mechanical properties of amylopectin are positively related to adhesion, films of the various amylopectin fractions were prepared and evaluated in the XY-direction. The test results are summarized in Table XXI. The data revealed that the XY-tensile strength, ultimate elongation, and apparent Young's modulus were independent of molecular weight until it was reduced to a level below 39,000 $\underline{M}_w$, i.e., only Fraction DF-5-IH (17,000 $\underline{M}_w$) showed significantly reduced mechanical strength and elongation below that of the other seven molecular fractions of amylopectin. From this result coupled with the above adhesion behavior,

it may be concluded that the limiting factor of effective adhesion between cellophane films using amylopectins from aqueous solution was the mechanical strength and elongation of the amylopectin as the molecular weight was reduced below 39,000. The plateau adhesion in the amylopectin-cellophane system was insensitive to molecular weight provided (a) there was sufficient amylopectin present to overcome the surface irregularities of the substrate (ca. 1400 A. or 0.2 g./m.^{2}), and (b) that the molecular weight was sufficiently high to maintain satisfactory film strength and elongation.

TABLE XXI

MECHANICAL PROPERTIES OF AMYLOPECTIN FILMS AS A FUNCTION OF MOLECULAR WEIGHT

Amylopectin Fraction	Molecular Weight, $\underline{M}_w$ x 10^3	XY-Tensile, kg./cm.^{2}	Ultimate Elongation, %	Apparent Young's Modulus, kg./cm.^{2} x 10^{-4}
Whole, Amp 121	4780	474	3.63	2.97
DF-5, Excluded	511	488	3.45	2.95
DF-6-S11, Excluded	280	471	3.72	2.82
DF-5-L	241	465	3.38	2.74
DF-6	182	487	3.29	2.92
DF-6-SIII, Included	136	468	3.78	2.80
DF-5-VL	39	473	3.25	2.90
DF-5-IH	17	310	0.51	2.68

Since the adhesion and the mechanical properties of the 17,000 $\underline{M}_w$ adhesive film decreased concurrently it would be expected that the adhesive would fail in cohesion in the joint between the films. Such did not appear to be the case, since the fracture zones upon observation displayed the identical fracture pattern

as that of the other amylopectin bonds where failure appeared as though it were of the scattered adhesive type (cf. Fig. 13). Nevertheless, as noted earlier, it is possible that failure was initiated in cohesion in an undetectable region and that the zone of failure was then transferred to the interface and propagated by a peel or cleavage mechanism to give the appearance of scattered adhesive failure. Thus, although many writers in the field of adhesion feel that cohesive failure mechanisms control ultimate joint strength, the location of the incipient center of failure is virtually impossible to determine in bonds as thin as those of this study.

Figure 18 shows the relationship between the extent of cellophane surface failure in cohesion as a function of the strength of the cellophane-amylopectin-cellophane bond (cf. Fig. 14). In spite of considerable scatter of the data it is evident that the amylopectin fractions of reduced molecular weight tended to cause more cellophane failure at comparable adhesion levels than did the whole amylopectin. Although molecular interpretation of this behavior is impossible to assess, it may be suggested that the low molecular weight fractions penetrated the substrate to a greater extent which resulted in greater failure of cellophane. Without significant molecular penetration, fracture or cleavage between the starch and the cellophane would be easier once initial failure occurred anywhere in the bond.

Effect of Diffusion of Amylopectin on Adhesion

The above results indicated that there was a loss of amylopectin from the surfaces of the cellophane films during drying of bond assemblies. Experiments were carried out to assess the quantitative relationships between the extent of amylopectin diffusion and cellophane adhesion.

Figure 19 illustrates the effect of amylopectin molecular weight on the extent of diffusion of amylopectin into the two cellophane films during bond formation. The procedure used was described on page 71 and the diffusion data are presented

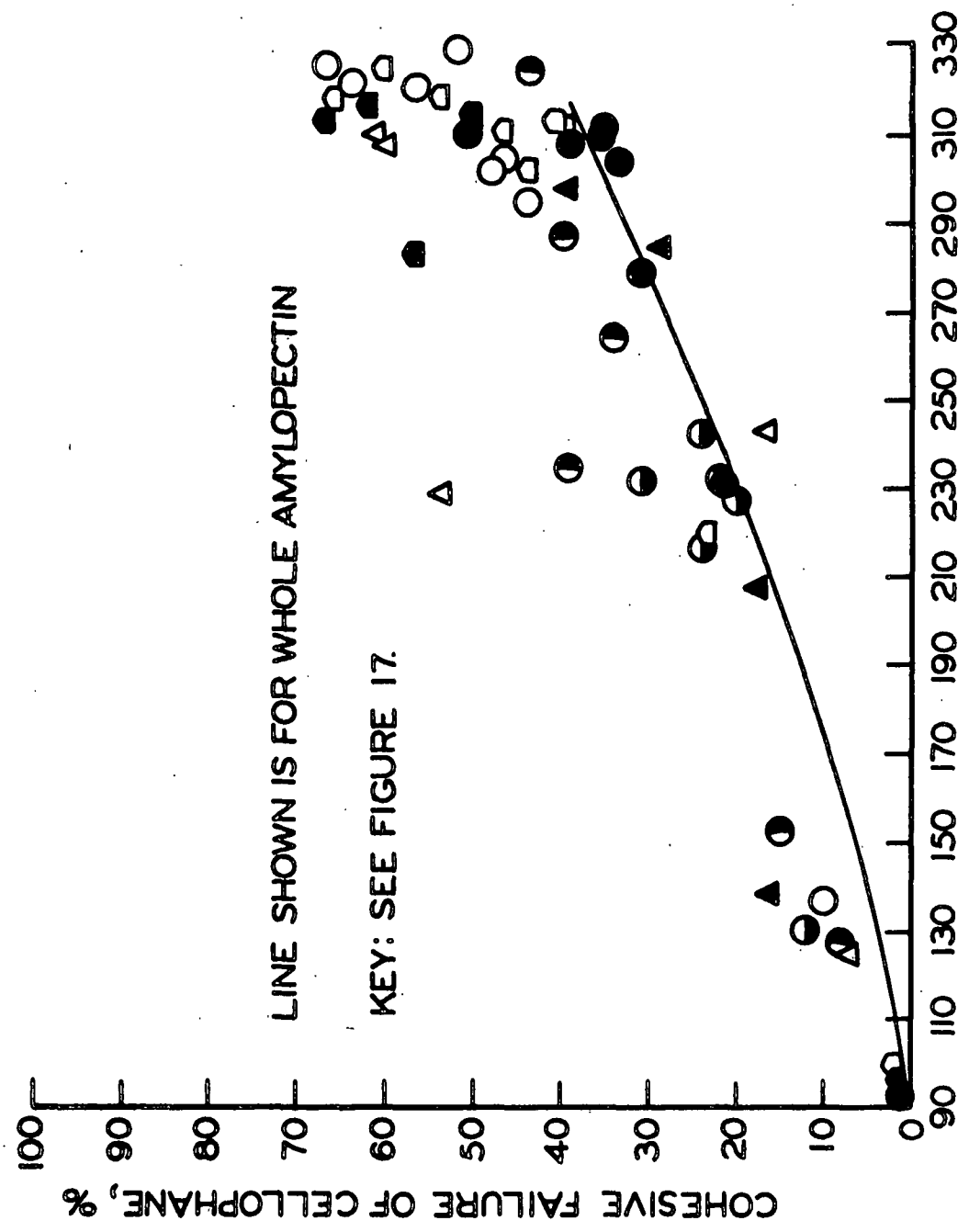


Figure 18. Relationship Between Effective Adhesion and Cohesive Failure of Cellophane for Various Fractions of Amylopectin

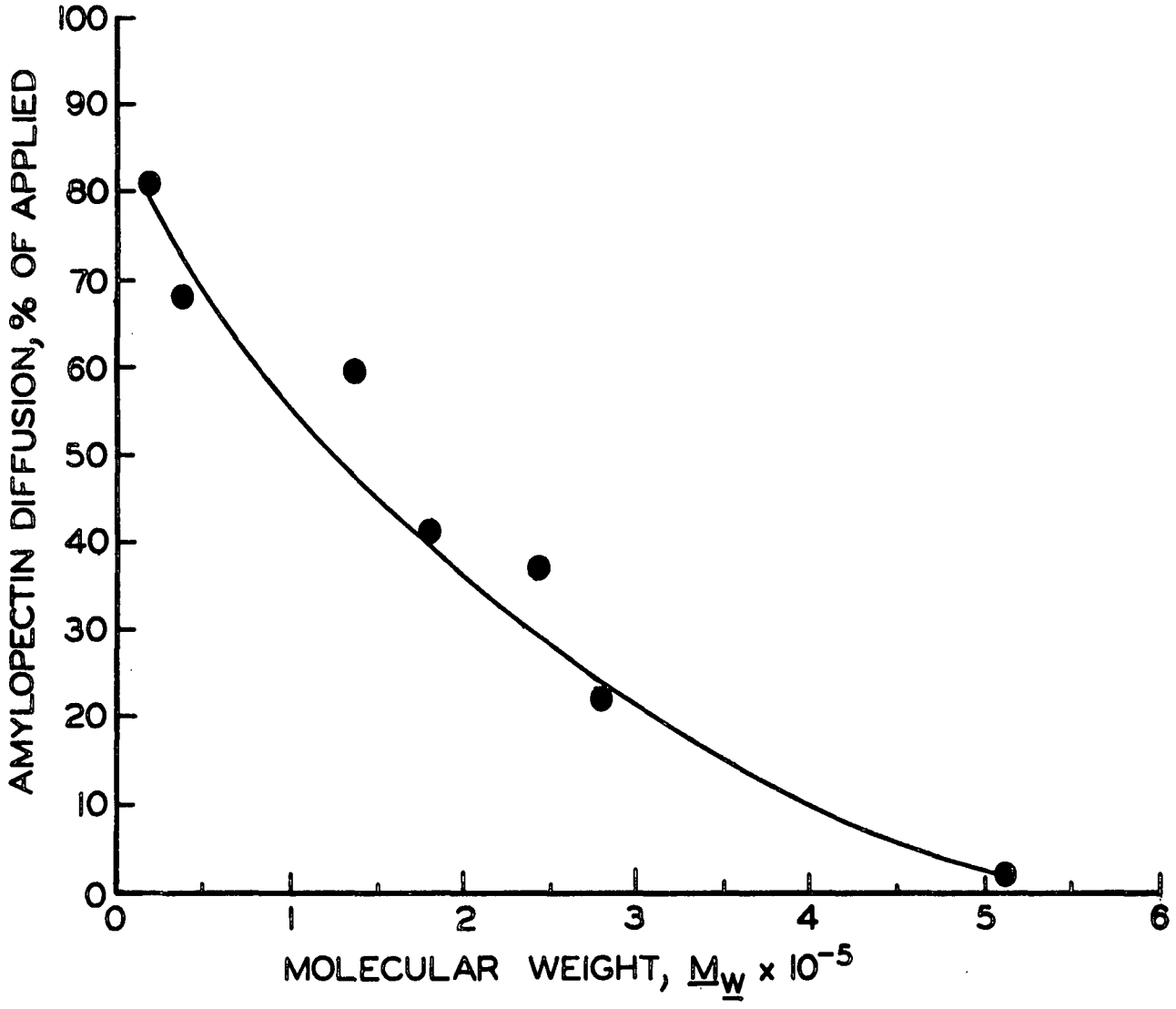


Figure 19. Relationship of Molecular Weight of Amylopectin and its Diffusion into Cellophane During Bond Preparation

in Appendix XII. The extent of amylopectin migration into the substrates was linearly related (as a first approximation) to the weight average molecular weight over a range of about 50,000 to 250,000. From 25 to 70% of the amylopectin present in the bond system was within the cellophane and not available to the interfacial zones of the bond. When the molecular weight exceeded about 500,000, no measurable amounts of amylopectin were lost to the adherends, although iodine staining showed that a trace of migration occurred even with whole amylopectin. Also, it was found (Appendix XII) that the higher the molecular weight of the diffused amylopectin fraction, the more difficult it was to extract. Since the light-scattering studies (Table XIX) revealed that this molecular weight corresponded to an average dimension of ca. 650 A., it indicates indirectly that the surface pores of the water-swollen cellophane used in this investigation are of this same order of magnitude.

By using the experimentally determined values for extent of diffusion of each amylopectin fraction, it was possible to correct the data of Table XX to yield, in each case, the amount of amylopectin remaining between the cellophane films. These corrected data are tabulated in Table XXII and are shown in Fig. 20. A comparison of Fig. 20 and 17 clearly shows that correction for the amount of amylopectin lost due to diffusion had a significant effect only on the three lowest molecular weight fractions. Considering only the bond, amylopectin makes the initial slope of all of the plots very steep and very comparable, illustrating again the effectiveness of all starch fractions in filling in the imperfections of the two surfaces and bridging the voids between them.

Sharp leveling off to the plateau adhesion level was not observed with M_w fractions 182,000 and 136,000. This could be attributed to the somewhat indirect nature of the correction for amount of amylopectin diffused. Any explanation in

TABLE XXII

CELLOPHANE ADHESION AS A FUNCTION OF VARIOUS AMYLOPECTIN MOLECULAR FRACTIONS AND AMOUNT OF AMYLOPECTIN BETWEEN THE CELLOPHANE

Amylopectin fraction	Effective Adhesion, kg./cm.^{2}							
	Whole Amp-121	DF-5-Excluded	DF-6-S-II	DF-5-L	DF-6	DF-6-S-III	DF-5-VL	DF-5-I H
Molecular weight, $\overline{M}_w \times 10^{-3}$	4780	511	280	241	182	136	39	17
Diffusion, %[a]:	0	2	22	37	41	59	68	81
Amount Amylopectin in Bond, between films, g./m.^{2}								
0.0 (control)	93 (1)	95 (2)	92 (1)	94 (1)	92 (2)	93 (1)	93 (1)	94 (1)
0.03	--	--	--	137 (10)	125 (7)	--	128 (8)	130 (12)
0.04	--	219 (23)	--	--	--	--	--	--
0.06	--	--	--	--	229 (54)	140 (16)	152 (15)	--
0.075	--	310 (47)	--	--	--	--	--	--
0.10	231 (21)	324 (60)	--	--	--	--	--	--
0.12	--	--	313 (67)	--	--	--	--	216 (24)
0.13	--	--	--	294 (44)	--	--	--	--
0.19	--	--	--	--	--	--	235 (39)	--
0.20	--	312 (41)	--	--	--	--	--	--
0.25	--	--	--	--	--	208 (18)	--	--
0.30	308 (36)	--	--	--	--	--	--	232 (31)
0.35	--	--	--	--	307 (60)	--	264 (34)	--
0.40	--	--	--	325 (67)	--	--	--	--
0.50	--	--	316 (62)	--	--	--	--	--
0.60	312 (35)	317 (66)	--	--	--	284 (29)	--	233 (22)
0.90	--	--	--	--	309 (61)	--	--	--
0.95	--	--	--	320 (57)	--	--	--	--
1.0	--	--	--	--	--	--	287 (40)	--
1.1	303 (34)	--	--	--	--	--	--	228 (20)
1.3	--	--	314 (50)	--	--	--	--	--

[a]See end of table for footnote.

TABLE XXII (Continued)

CELLOPHANE ADHESION AS A FUNCTION OF VARIOUS AMYLOPECTIN MOLECULAR FRACTIONS AND AMOUNT OF AMYLOPECTIN BETWEEN THE CELLOPHANE

Amylopectin fraction	Effective Adhesion, kg./cm.^{2}							
	Whole Amp-121	DF-5-Excluded	DF-6-S-II	DF-5-L	DF-6	DF-6-S-III	DF-5-VL	DF-5-I H
Molecular weight, $\underline{M}_w \times 10^{-3}$	4780	511	280	241	182	136	39	17
Diffusion, %[a];	0	2	22	37	41	59	68	81
Amount Amylopectin in Bond, between films, g./m.^{2}								
1.4	--	--	--	--	--	--	--	242 (24)
1.5	310 (51)	--	--	--	--	--	--	--
1.6	--	--	--	321 (64)	--	--	--	--
1.8	--	--	--	329 (52)	--	--	--	--
2.0	--	--	--	302 (48)	--	--	--	--
2.3	307 (39)	--	--	--	--	297 (40)	--	--
2.4	--	--	--	--	--	--	324 (44)	--
2.5	--	--	--	--	--	--	--	--
2.7	--	318 (54)	--	--	--	--	--	--
2.8	--	--	--	--	--	--	--	--
3.0	--	312 (40)	--	--	--	--	--	--
4.8	--	--	--	304 (47)	--	--	--	--
5.5	--	--	--	--	--	--	--	--
7.5	--	301 (44)	--	--	243 (16)	--	--	--
7.8	--	--	282 (57)	--	--	--	--	--
8.8	279 (31)	--	--	--	--	--	--	--

[a] Diffusion of amylopectin into cellophane as evaluated by technique described on p. 71.

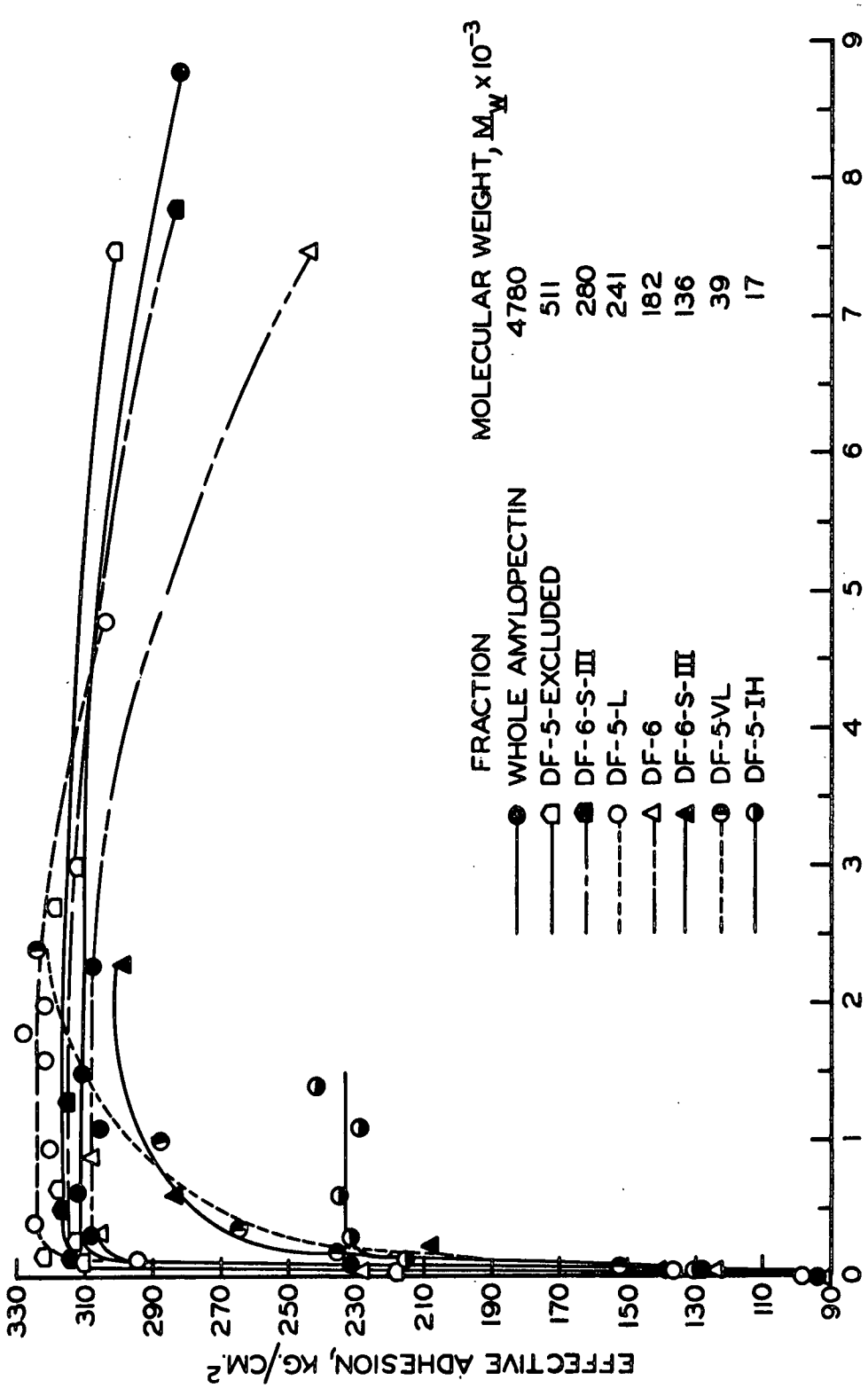


Figure 20. Effective Adhesion of Various Amylopectin Fractions as a Function of Amylopectin Content Between the Films

terms of molecular effects does not seem realistic because the lowest molecular weight fraction of the three exhibited a sharp break in the curve to the plateau level.

Table XXIII summarizes the relationships for the various amylopectin fractions between diffusion, adhesion, and cohesive cellophane rupture. For the first five fractions of decreasing molecular weight and increasing diffusion, the degree of cellophane cohesive rupture upon bond failure increased slightly from about 40% for whole amylopectin to 60% for the third through fifth fractions. The three amylopectins of lowest molecular weight showed the highest degree of diffusion, but the extent of cellophane failure decreased. Also, only the very lowest molecular weight fraction, showed a significant decrease in level of plateau adhesion accompanied by a marked lessening of cellophane failure.

TABLE XXIII

RELATIONSHIP OF AMYLOPECTIN DIFFUSION, ADHESION, AND COHESIVE FAILURE OF CELLOPHANE

Amylopectin Fraction and $\underline{M}_w$ x 10^{-3}	Diffusion of Amylopectin, %	Plateau Adhesion, kg./cm.^{2}	Cohesive Failure of Cellophane in Plateau Region, %
Whole, 4780	0	308	39
DF-5-Ex., 511	2	315	51
S-II, 280	22	314	60
DF-5-L, 241	37	324	60
DF-6, 182	41	308	60
S-III, 136	59	301	40
DF-5-VL, 39	68	324	44
DF-5-IH, 17	81	234	24

Even though diffusion and extent of cellophane rupture increased, plateau or maximum adhesion remained essentially constant at 308 to 324 kg./cm.^{2}. This indicates either (a) that the interfacial contact of amylopectin to cellophane is optimum, even in the case of whole amylopectin with no gross diffusion, and that any increase in contact through greater diffusion merely results in changing the nature and/or location of the failure zone, or (b) that the "weak-link" of the bond system is the cellophane substrate. It should be recalled (Table XVII) that the Z-direction tensile strength of cellophane was 322 kg./cm.^{2} as compared with 236 kg./cm.^{2} for amylopectin. Since three-layered bonds potentially have greater ability to absorb energy and distribute stresses than the single-layered films used for the evaluation of Z-tensile, these Z-direction strengths are probably minimum values. Cellophane appears to be stronger than amylopectin, but this could be reversed if the thickness of the amylopectin films could be reduced to correspond to that found in the plateau region of adhesion (viz. 0.2 to 2 g./m.^{2} or 0.14 to 1.4 μm.). Therefore, it is very difficult to determine unequivocally whether failure in the plateau region is due to cohesive cellophane failure or to cohesive failure of the amylopectin.

One may argue that the increased diffusion improved adhesion while the lowered molecular weight decreased adhesion. This could result in a compensation of effects and, therefore, the observed constant bond strength. In order to separate the contributions of molecular weight and diffusion, six sets of bonds were prepared with amylopectin DF-5-L ($\underline{M}_w$ = 241,000) wherein the extent of diffusion was altered by varying (1) the length of time the bond assembly was stored prior to drying and (2) the rate of drying.

The results summarized in Table XXIV show that there was no significant change in apparent adhesion or in the degree of cohesive failure of cellophane as a result of increasing the extent of diffusion of amylopectin from 16 to 52%, provided

TABLE XXIV

EFFECT OF AMYLOPECTIN DIFFUSION ON BOND STRENGTH[a]

Code	Time Stored Prior to Drying, hr.[b]	Drying Time, min.	Amylopectin, g./m.^{2}				Effective Adhesion, kg./cm.^{2}[e]	Cohesive Failure of Cellophane, %
			Between Films	Diffused[d]	Total	Diffused, % of applied		
115-A	0	22[c]	4.13	0.78	4.91	16	305	48
115-B	0	125	3.34	1.44	4.78	30	325	52
115-C	1	125	2.67	2.18	4.85	45	304	44
115-D	24	125	2.34	2.54	4.88	52	312	59
115-E	0	22	0.168	0.032	0.20	16[f]	309	49
115-F	24	125	0.096	0.104	0.20	52[f]	246	28

[a] Used amylopectin DF-5-L, $\overline{M}_w$ of 241,000; externally preroughened cellophane. Applied 5.0 g./m.^{2} of amylopectin (10 ml.).

[b] Stored by sealing in polyethylene.

[c] Used fan.

[d] Mean of three determinations.

[e] Mean of eight determinations.

[f] Estimated from Sets 115-A and 115-D.

sufficient amylopectin remained between the films to form a continuous film (i.e., 0.15 g./m.^{2}). Bond 115-F was significantly low in both adhesion and degree of cohesive failure of cellophane because insufficient amylopectin remained between the films.

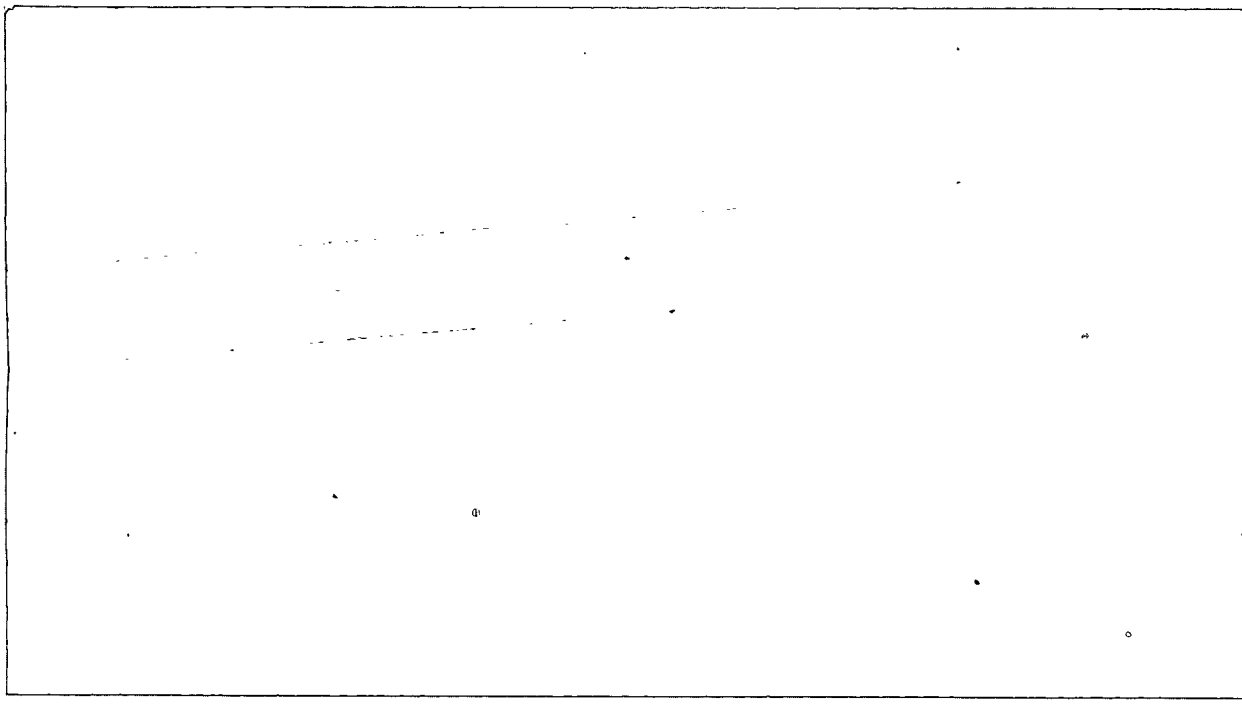
It is evident from Tables XXIII and XXIV, that gross diffusion of amylopectin was not necessary to obtain high levels of adhesion. After correction for diffusion loss, adhesion in these experiments was insensitive to molecular weight unless the amylopectin was severely degraded to the point where mechanical properties were seriously reduced.

The extent of amylopectin diffusion did not appear to be consistently related to the extent of cellophane rupture, even though part of the data of Table XXIII indicated a positive relationship. Again this points up the difficulty associated with interpreting bond fracture patterns and mechanisms on a molecular level.

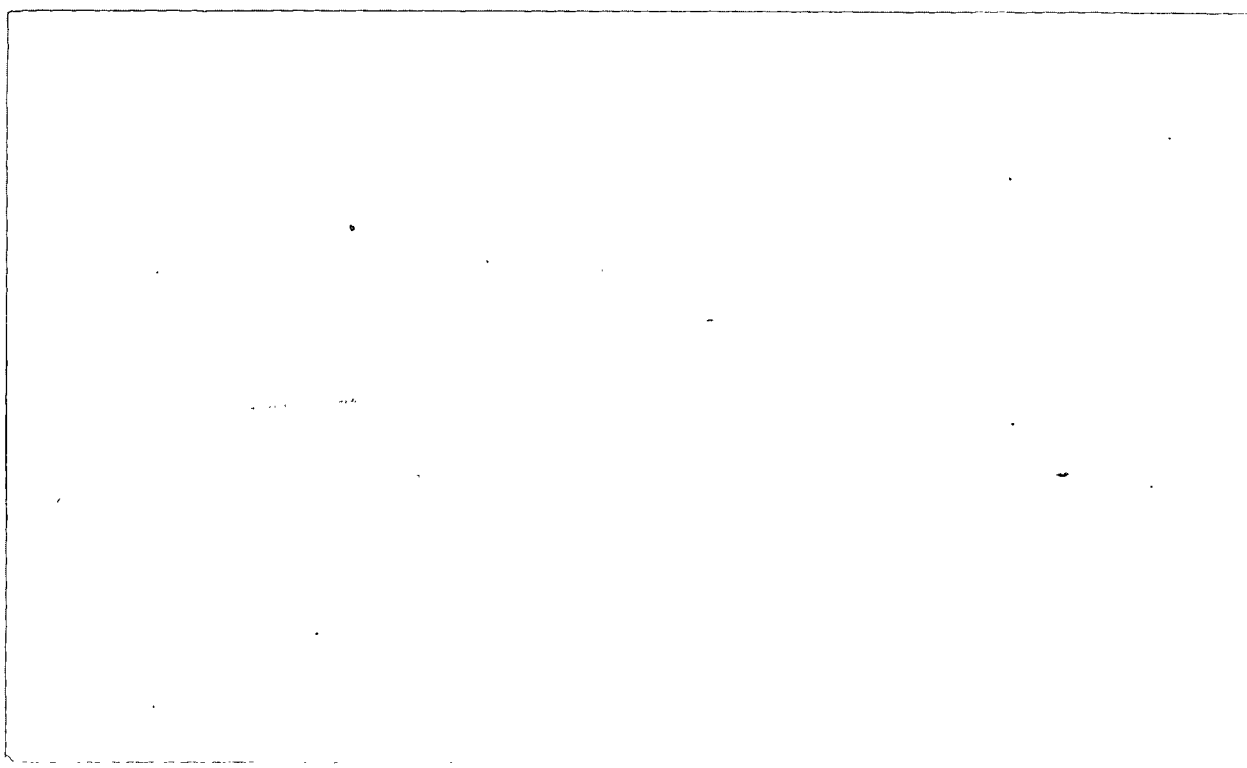
Photographic evidence of the extensive diffusion of amylopectin during bond formation is presented by photomicroscopy of bond cross sections. Figure 21A illustrates the excellent interfacial contact of two cellophane films bonded with 5.5 g./m.^{2} of amylopectin. When this same bond was stained with iodine-potassium iodide solution (Fig. 21B), the presence of both bond and diffused amylopectin could be observed. In Fig. 22 the upper film only was leached in hot water to remove the diffused amylopectin. Both films were then stained with iodine reagent. The contrast between the upper and lower films indicated the extent of amylopectin diffusion which, in this case, was distributed throughout the entire thickness of the cellophane film, as well as concentrated at the interface.

Effect of Molecular Weight of Amylose on Its Adhesion Behavior

It was shown (Fig. 10) that amylose yielded adhesion maxima comparable to amylopectin, but that it was much more sensitive to adhesive film thickness.



A. Not Stained with Iodine; 110X Magnification



B. Stained with Iodine; 210X Magnification. (Note: 2.4 g./m.^{2} of Amylopectin in Bond Between Films, 3.1 g./m.^{2} Diffused Into Film)

Figure 21. Photomicrographs of Cross Section of a Cellophane-Amylopectin-Cellophane Bond. Amylopectin, 136,000 $\underline{M}_w$. Section Thickness 20 μm.

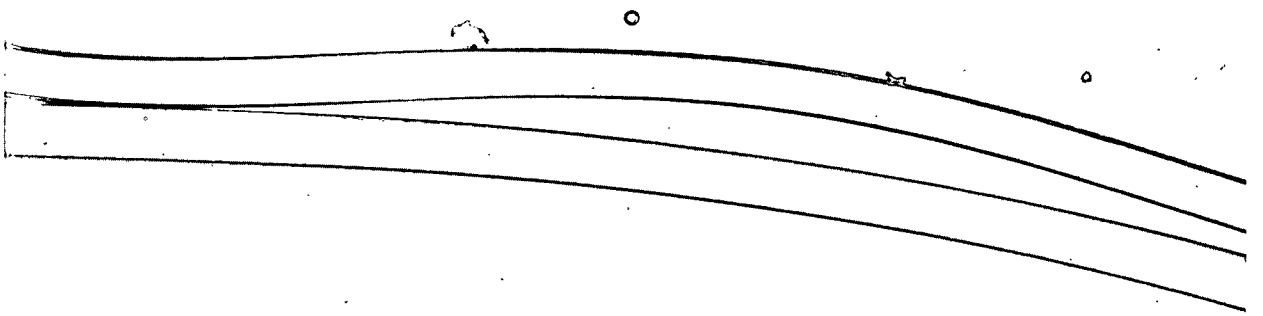


Figure 22. Photomicrograph of Cross Section of Two Cellophane Films Which Had Comprised a Bond with Amylopectin. Films Separated When Wet. Upper Film only Leached in Hot Water. Both Films Stained.

Magnification: 110X
Section Thickness: 20 μm.
Stain: I-KI
Amylopectin: 136,000 $\underline{M}_w$ 5.5 g./m.^{2}
Total Present in Initial Bond

Cleavage- or peel-type failure at reduced adhesion level was often observed (Fig. 12). It was the purpose of this portion of this study to investigate molecular weight effects to determine the cause for this phenomenon.

Three amylose fractions of decreased molecular weight were prepared by mild acid hydrolysis under helium (cf. p. 181). Light-scattering molecular weights and dimensions were measured and are reported in Table XIX. Four fractions of amylose were available for adhesion study of molecular weight: 1.1 million (whole amylose), 430,000, 252,000, and 70,000.

A series of amylose-cellophane bonds was prepared with the most highly degraded amylose. Effective adhesion level was found to be very low (ca. 140 kg./cm.^{2}) over the entire range of adhesive film thicknesses investigated (0.1 to 3.8 g./m.^{2}). In addition, most failures were of the peel type where most of the starch film was found on one of the cellophane surfaces. Low adhesion and peel failure in this series of bonds could not be attributed to high amylose film thickness per se, since very thin adhesive films were involved.

A clue to the low level of adhesion in this system was provided by the observation of the extreme tendency for this low molecular amylose to retrograde. Freshly prepared bond assemblies (cellophane-amylose solution-cellophane) displayed a marked loss in transparency in a matter of minutes, as very rapid retrogradation of the amylose solution between the films occurred. This observation strongly indicated that rapid retrogradation could be a large factor in the observed sudden decrease of adhesion in the whole amylose.

Figure 10 showed that for whole amylose a sudden decrease in bond strength occurred between 0.8 and 2.2 g./m.^{2} of amylose coverage. Since the standard procedure for preparing the bonds was to change the amylose concentration while maintaining constant volume, the above range of coverage also corresponded to an amylose concentration difference of 0.9 to 2.3 g./dl. Because the rate of retrogradation is dependent strongly on concentration (cf. Fig. 16), it is quite conceivable that the observed sudden decrease in amylose-cellophane adhesion was due to rapid retrogradation caused by high amylose concentration rather than to film thickness. In order to test this mechanism, the experiments summarized in Table XXV were performed, wherein the concentration of whole amylose was changed by a factor of 2.4 (through the region of concentration which appeared critical, based on the previous results) while the film thickness was maintained at 2.0 g./m.^{2}. This quantity of amylose corresponded to maximum adhesion for whole amylose.

TABLE XXV

EFFECT OF WHOLE AMYLOSE CONCENTRATION ON ADHESION OF CELLOPHANE

Code	Amylose Concn., g./dl.	Amylose Volume, ml.	Bond Area, $m.^2$	Amylose in Bond, $g./m.^2$	Effective Adhesion, $kg./cm.^2$
1-A	2.16	5.0	0.054	2.00	219
1-B	0.90	12.0	0.054	2.00	278
2-A	2.16	5.0	0.054	2.00	211
2-B	0.90	12.0	0.054	2.00	287
C (control)	0.874	5.0	0.054	0.81	302

It is evident from Table XXV that the dilute amylose solutions resulted in bonds possessing significantly higher adhesion than did the concentrated solutions. Because it had been observed that variations in volume and concentration has no effect on adhesion in the amylopectin system (where retrogradation is absent), the concentration dependent retrogradation mechanism for amylose is supported. The use of dilute amylose solutions enabled the preparation of thick amylose bonds (Code 1-B) of strength in the order of 280 $kg./cm.^2$ and avoided peel failure.

The two remaining hydrolyzed amylose fractions were then evaluated for adhesion and film strength. The results for all amylose fractions are summarized in Table XXVI. It is noted that the maximum adhesion decreased with decrease in molecular weight of the amylose in spite of the fact that the mechanical properties of the free films were essentially constant, (with the exception of the most degraded fraction). In contrast, maximum adhesion appeared to be inversely related to the rate of retrogradation of the amylose solutions used. The lower the molecular weight, the more rapidly the amylose retrograded and the lower the maximum adhesion. Interestingly, the peel-type of adhesive joint failure, which resulted from use of

TABLE XXVI

SUMMARY OF ADHESION AND FILM DATA FOR AMYLOSE FRACTIONS

Amylose Fraction	$\bar{M}_w$	Time for 0.5 g./dl. Solution to Retrograde Visually, min.[a]	X-Y Tensile, kg./cm.^{2}	Elongation, %	Z-Tensile, kg./cm.^{2}	Effective Adhesion, kg./cm.^{2}	
						Maximum	Peel-Type[b]
Whole	1,100,000	450	533	13.9	193	301	222
Hydrolyzed 0.5 hr.	430,000	120	523	13.0	199	275	228
Hydrolyzed 1.0 hr.	252,000	35	528	12.8	184	221	215
Hydrolyzed 3.0 hr.	70,000	5	312	5.3	--	164	164

[a] Normally, 90 minutes required to evaporate free water during bond preparation.

[b] Maximum represents plateau adhesion level; peel-type failure resulted from use of relatively high concentrations of amylose for bond preparation.

high concentration levels of amylose, occurred in the range of 225 kg./cm.^{2} for all but the most highly hydrolyzed amylose. Here both maximum and peel-type adhesion failure occurred at 164 kg./cm.^{2}. This low level of adhesion exhibited by the highly hydrolyzed amylose may be attributed to the corresponding loss in both ultimate strength and elongation for free films of the 3.0-hour-hydrolyzed amylose, in addition to the extremely rapid rate of retrogradation.

A brief explanation of the mechanism by which rapid retrogradation may reduce adhesion follows. Amylose will retrograde to some extent during the preparation of all cellophane bonds, no matter how dilute the initial solution, because the solution becomes progressively more concentrated as the bonds dry. Since 90 minutes were required to evaporate the free liquid during bond preparation, considerable time was available for retrogradation. If retrogradation occurs very rapidly as in the case of relatively concentrated solutions and/or low molecular weight amylose, the adhesive molecules very probably become inactivated by internal satisfaction of secondary attractive forces and their rate of movement and relative mobility decreases due to the increase in effective size of the particles. Both of these processes would reduce molecular orientation and interaction at the cellophane surface, resulting in lower levels of adhesion.

Furthermore, smaller molecules can align more readily because of their more rapid molecular transport and because they have less tendency to associate intramolecularly (128). Because of this, low molecular weight amylose molecules would tend to form crystals which were more closely associated and less reactive in adhering to another surface, such as cellophane. To determine whether this hypothesis was tenable, x-ray diffraction analyses were carried out on films of whole and 3.0-hour hydrolyzed amyloses. The technique employed was described earlier. The x-ray diffraction patterns are given in Appendix XIII along with that of amylopectin for comparison, which typically gave an amorphous pattern. Table XXVII indicates that

the crystallinity index of the hydrolyzed amylose was slightly greater than that of the whole fraction. Table XXVIII summarizes a separate experiment in which an amylose solution was allowed to retrograde for several days prior to using it to prepare a cellophane bond and, in parallel, to cast a film of amylose. Adhesion at the plateau region was reduced by 25% by permitting retrogradation to occur prior to bond preparation, even though the mechanical properties of the film were affected very little. Retrograded amylose bonds also failed by total peel of the amylose from one of the adherends. Similar low level adhesion and peeling results were obtained with retrograded amylose, regardless of whether retrogradation occurred externally prior to bond preparation or internally during the standard evaporation process of bond formation.

TABLE XXVII

CRYSTALLINITY INDEX OF AMYLOSE FILMS

Amylose Fraction	Transmission $\underline{T}_{Minimum}$	Transmission $\underline{T}_{Maximum}$	Intensity[a] $\underline{I}_{Maximum}$	Intensity[a] $\underline{I}_{Minimum}$	Crystallinity Index, C.I., %[b]
Whole	23	53	0.638	0.275	56.8
Whole	30	58	0.523	0.235	55.1
Hydrolyzed, 3 hours	10.5	49	0.981	0.302	69.2
Hydrolyzed, 3 hours	14	52	0.853	0.286	66.5

[a] $\underline{I} = \log (100/\underline{T})$.

[b] $\underline{C.I.} = (\underline{I}_{max.} - \underline{I}_{min.})/\underline{I}_{max.} \times 100$.

Figures 23 and 24 compare the appearance after iodine-staining of a strong amylose-cellophane bond with that of a weak one which exhibited peel-type failure. Figure 23 shows the typical fracture pattern of a strong amylose bond with amylose distributed between both cellophane films following rupture. Considerable cohesive

failure of cellophane is evident. Figure 24 shows typical peel failure of a weak bond with most of the amylose remaining on one adherend. Special notice should be taken of the mottle pattern of the amylose which was the result of considerable retrogradation of the amylose solution before the bond was formed.

TABLE XXVIII

EFFECT OF AMYLOSE RETROGRADATION ON ADHESION AND AMYLOSE FILM PROPERTIES

Amylose	Adhesion Plateau, kg./cm.^{2}	Amylose Film Properties			Apparent Young's Modulus, kg./cm.^{2} x 10^{-4}
		XY-Tensile, kg./cm.^{2}	Z-Tensile, kg./cm.^{2}	Ultimate Elongation, %	
Whole	310	533	191	13.9	3.12
Retrograded highly	231	522	185	12.4	3.01
Retrograded, internally[a]	221	--	--	--	--

[a] From Table XXVI.

The effect of rate of loading on effective adhesion was discussed on p. 80. The mechanism of failure was determined by extent of amylose peel and degree of cohesive failure of the cellophane was unchanged by the rate of loading. The fact that low rates of loading, which favor ductile (shear) type of fracture, did not increase the extent of peel failure, even for amylose thicknesses over 1 μm. was strong evidence against this explanation for peel-failure, and renders the retrogradation process discussed above more probable for explaining the low adhesion of thick amylose bonds.

Iodine staining of amylose-cellophane bonds after testing indicated that even the lowest molecular weight fraction of amylose (70,000) did not diffuse into the substrate. This is in direct contrast to amylopectin which showed marked diffusion

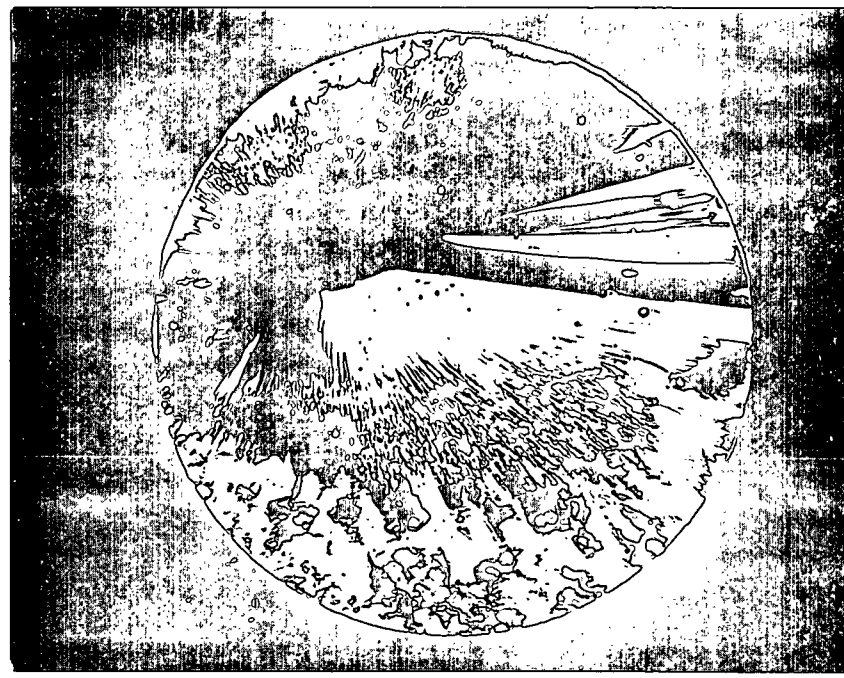


Figure 23. Top View of a Strong Amylose-Cellophane Bond After Failure Showing Typical Shatter-Lines and Cohesive Failure of Cellophane. Iodine Stained and Magnified Three Diameters

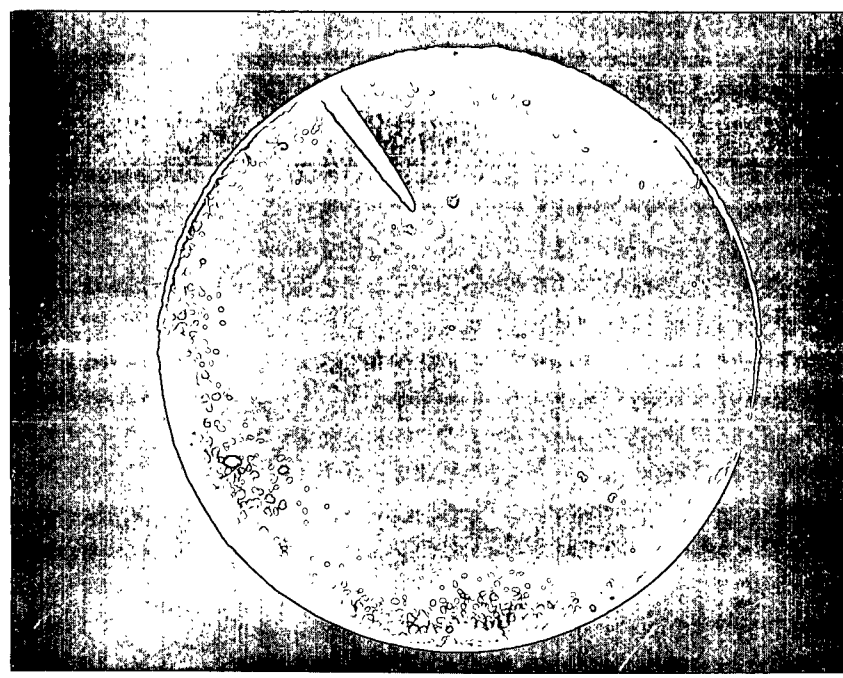


Figure 24. Top View of a Weak Amylose Cellophane Bond After Failure Showing Peel-Type Failure and Mottle Due to Retrogradation. Stained with Iodine and Magnified Three Diameters

at all molecular weights below 500,000. Figures 5 and 25 are photomicrographs of bond cross sections giving visual proof of the lack of amylose diffusion into the cellophane. Figure 5 indicates that all of the amylose was concentrated between the films, even though the amylose was of very low molecular weight (70,000). This cross section should be contrasted to that of Fig. 21B showing marked diffusion for amylopectin of molecular weight 136,000. Figure 25 shows that the amylose film has a marked tendency to peel from the cellophane, which indicated that as a result of retrogradation amylose molecules have a greater tendency to cohere to themselves rather than to adhere to the cellophane. Figure 25 also shows the total lack of amylose diffusion during bond formation.

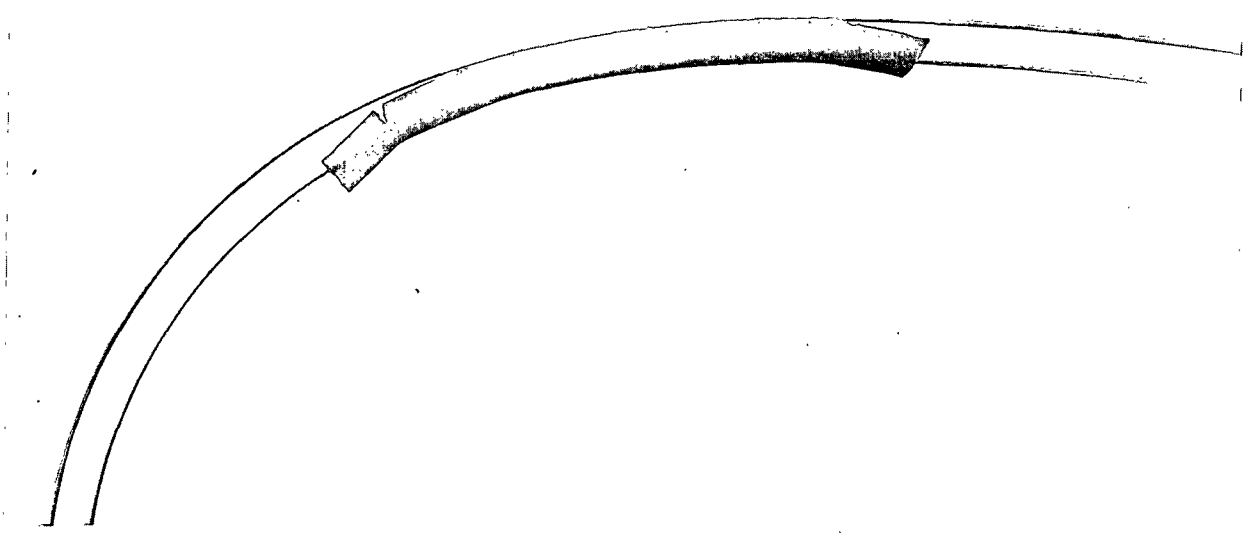


Figure 25. Photomicrograph of Top View of a Single Cellophane Film Cross Section Showing Amylose Film Partially Detached from Cellophane Surface. Absence of Gross Diffusion of Amylose is Evident. (Note: This View Corresponds to a 90° Difference from Fig. 5, and is Actually the Width of the Microtome Section)

Magnification: 110X; Section Thickness: 20 μm.; Stain: I-KI; Amylose: 70,000 $\underline{M}_w$, 3.3 g./m.^{2}

ADHESION OF STARCH-CELLOPHANE AS AFFECTED BY ABRASION AND SOLVENT CLEANSING OF CELLOPHANE

It was shown earlier (p. 97) that solvent cleansing and abrasion of the substrate had a significant effect on cellophane adhesion when bonded from water. This final section of experimental results presents the experiments carried out with amylose and amylopectin adhesion as affected by solvent cleansing and abrasion of the substrate.

Relationship Between Adhesion, Diffusion of Adhesive, and Solvent Cleansing of Substrate

Table X showed that the use of solvent-cleansed cellophane caused a 20% increase in cellophane-to-cellophane adhesion in the water system as compared to uncleaned cellophane. On the basis of this observation the question arises whether this effect of contamination of the cellophane will carry over into cellophane adhesion with starch fractions.

Table XXIX summarizes the experiments made with amylose and amylopectin using solvent-cleansed and uncleansed cellophane. All four sets of specimens showed a highly significant decrease in effective adhesion and in extent of cohesive failure of cellophane as a result of contaminated cellophane. The amylose bonds which exhibited no diffusion into the substrate showed a greater percentage decrease in adhesion (ca. 30%) than did the amylopectin (ca. 20%) which displayed considerable diffusion. From this it may be concluded that the adhesion in the starch-water-cellophane system is primarily of the specific type, i.e., involving intermolecular attraction between adhesive and adherend. Since diffusion of the amylopectin apparently reduced the deleterious effect of surface contamination the mechanical adhesion theory (p. 35) cannot be totally ignored. However, in view of the fact that about 20% decrease in adhesion occurred with the uncleaned cellophane, even though 2 to 5 g./m.^{2} of amylopectin diffused into the substrate, one must conclude

TABLE XXIX

EFFECT OF SOLVENT CLEANSING OF CELLOPHANE ON STARCH DIFFUSION AND CELLOPHANE ADHESION

Starch Code	Starch Fraction	Amount of Starch[a], g./m.^{2} Between Films	Diffused into Films	Total	Diffused, % of total	Effective Adhesion, kg./cm.^{2}	Cohesive Failure of Cellophane, %	Decrease in Adhesion, %
Solvent-Cleansed Cellophane								
117-A	Amylopectin DF-6	1.15	0.95	2.00	45[b]	310	53	--
117-B	Amylopectin DF-6	2.77	2.34	5.21	45	318	57	--
117-C	Whole Amylose-B	0.14	0.00	0.14	0	282	50	--
117-D	Whole Amylose-B	0.81	0.00	0.81	0	305	51	--
Uncleansed Cellophane								
117-E	Amylopectin DF-6	1.24	1.00	2.24	40[b]	251	34	19
117-F	Amylopectin DF-6	3.05	2.04	5.09	40	238	31	25
117-G	Whole Amylose-B	0.14	0.00	0.14	0	193	14	32
117-H	Whole Amylose-B	0.81	0.00	0.81	0	202	14	34

[a]Amylopectin DF-6, $\underline{M}_w$ = 182,000.

[b]Values assumed from evaluation of 117-B and 117-F, respectively.

that mechanical interlocking effects play, at best, a secondary role in this system. Furthermore, the small gain in adhesion which apparently resulted from the diffusion could be attributable to an increase in area of molecular contact between adhesion and adherend rather than to any mechanical interlocking per se.

Effect of Surface Abrasion of Cellophane on Adhesion with Starch

Work with cellophane adhesion with water only has shown (Table XV) that adhesion could be increased up to 60% by roughening the surfaces of cellophane prior to bonding. The reader will also recall that abrasion assisted markedly the adhesion in the systems cellophane-epoxy adhesive and starch film-epoxy adhesive.

Preliminary experiments on adhesion in the amylopectin-cellophane system showed that abrasion of the surfaces involved in the bonds caused a significant reduction in apparent adhesion when there was sufficient starch present to attain the maximum plateau region. This somewhat surprising observation was confirmed by additional experimentation with both whole amylopectin and whole amylose. The data are summarized in Table XXX.

With both amylose and amylopectin, adhesion was decreased from 14 to 25% by the abrasion of the cellophane surfaces before the bonds were prepared. Furthermore, abrasion changed the nature of failure in that the extent of cohesive rupture of the cellophane in the plateau region increased to ca. 95% as compared to ca. 50% in the case of nonabraded cellophane. The most plausible explanation for this is that abrasion may introduce discontinuities and, hence, regions of stress concentration at the interface between the cellophane and starch. Of course, one might say that roughening of cellophane reduced its resistance to tensile stress, but this, in itself, could not explain the low levels of bond strength because Z-direction cohesion measurements carried out on single abraded-cellophane films yielded high strengths of ca. 320 kg./cm.^{2}.

TABLE XXX

EFFECT OF ABRASION OF CELLOPHANE ON ADHESION WITH AMYLOSE AND AMYLOPECTIN[a]

Starch Fraction[b]	Starch in Bond, g./m.^{2}	Cellophane Surface[c]	Apparent Adhesion, kg./cm.^{2}	Cohesive Cellophane Failure, %	Decrease in Adhesion, %
Amylopectin	0.13	Smooth	229	21	--
	0.13	Abraded	183	68	20
Amylopectin	1.62	Smooth	310	51	--
	1.62	Abraded	268	99	14
Amylopectin	3.50	Smooth	321	56	--
	3.50	Abraded	236	97	26
Amylose	0.14	Smooth	282	50	--
	0.14	Abraded	238	93	16
Amylose	0.81	Smooth	309	51	--
	0.81	Abraded	244	98	21

[a]Cellophane films were solvent cleaned after abrasion using standard sequence.
[b]Whole fractions, prepared by standard technique of clarification.
[c]Abrasion was carried out using No. 303 emery dust and felt-backed brass plate; 350 strokes per side.

Thus, roughening of the adherend gave the following apparently contradictory results in this entire study:

1. Adhesion of cellophane using water alone was increased by 62% by prior roughening of the cellophane.

2. Adhesion between epoxy resin adhesive and cellophane was increased about 85% by roughening of the cellophane.

3. Adhesion between epoxy resin and films of amylose and amylopectin was increased significantly by preabrasion of the films.

4. Adhesion of the systems cellophane-starch-cellophane was reduced by about 20% by preroughening of the cellophane surfaces. All of the above facts may be interpreted on the basis of the relative mobility of the adhesive molecules and the relative availability of surface hydroxyl groups of the substrate.

In the first three instances, effective adhesion was probably increased by abrasion of the substrate because:

1. Roughening increased the degree of surface-to-surface contact between the two films. The surface mobility of water-swollen, unroughened cellophane apparently is small when compared to the gross size of the surface irregularities. Water molecules are so small that they possess very little gap-bridging ability between surface elements which are so widely separated as nonabraded films. Abrasion would allow closer approach of the surfaces by creating smaller structural elements possessing increased mobility and deformability and greatly facilitates increased bridging by water molecules.

2. and 3. Without abrasion of the cellophane or starch film surfaces, relatively few hydroxyl groups are available to the epoxy adhesive. The lack of reactive centers for adhesive-adherend interaction can be attributed to two factors: (a) the dry cellophane or starch films represent a relatively dense, well-packed system as compared to the water-swollen condition, and (b) the epoxy adhesive was pastelike in consistency which probably resulted in restriction of molecular mobility because of viscous drag and molecular entanglements. After reaction with the curing agent commences, cross-linking of the epoxy resin reduces the number of reactive centers in the adhesive which would be available for adhesion and, also, further reduces the flow of the adhesive. Evidence for the above is given by our experiments where adhesion of epoxy to cellophane was found to be very time dependent. A rapid decrease in bond strength was observed if the adhesive was not used within

15 minutes of elapsed time following blending of the curing agent. Alter (161) and Kumaran (162) both found a deleterious effect due to high solution viscosities of epoxy adhesives when used for adhesion to metal surfaces. Alter interpreted his results in terms of reduced polymer absorption at the interface, while Kumaran felt that the reduced mobility of the adhesive molecules prevented them from aligning on the adherend surface.

Based on the above considerations, hypotheses may be offered to explain why adhesion was decreased by abrasion of the adherend when starches were used. Because of their large molecular dimensions, amylose and amylopectin possess the gap-bridging ability which water lacks. Therefore, surface discontinuities and gaps amounting to several hundred angstrom units conceivably can be spanned by a single starch molecule, whereas gaps in the order of a thousand or more angstrom units may be bridged by layers of starch molecules. The dilute aqueous solutions of amylose and amylopectin used in these experiments were of low viscosity and hence possessed good molecular mobility, at least before extensive evaporation and/or retrogradation took place. If the gap-bridging potential and high mobility of the starch molecules are coupled with the use of water-swollen cellophane substrates, it is reasonable to postulate that there is sufficient intimate adhesive-adherend contact area to create optimum adhesion in this system without any prior surface abrasion of the cellophane. Thus, abrasion of adherends in the starch-cellophane system appeared to introduce stress concentration sites which were not sufficiently compensated for by increase in bonded area as in the case of the absence of starches. The occurrence of increased stress concentration was evidenced by the great increase in the extent of cohesive rupture of cellophane as well as by the reduced bond strength.

CONCLUSIONS

The basic conclusions of this study are presented in the same order as the hypotheses which were presented previously (p. 44).

1. Close contact of the cellophane adherends was the most critical factor in attaining high effective adhesion. The effectiveness of water as an adhesive was limited, but increased with abrasion of the adherends, drying under pressure, and by matching the direction of the extrusion lines on the cellophane surface. The various starch fractions were much more effective than water in establishing molecular "bridges" across the void spaces between the adherends.

2. Changes in the molecular weight of amylose and amylopectin affected adhesion through changes in (1) the final mechanical properties of the adhesives, and (2) the behavior of the adhesives during bond formation. Amylopectin adhesion was very insensitive to molecular weight decrease provided that its cohesive strength was preserved. On the other hand amylose was very sensitive to molecular weight decrease even though its cohesive strength was not affected.

3. The difference in adhesion behavior of amylopectin and amylose (see 2, above) was due to the marked tendency of amylose to associate (retrograde) in solution. Lower molecular weights favored more rapid association and higher crystallinity of the aggregates and, probably, made the molecules less available for adhering to and bridging across the cellophane adherends. The highly branched amylopectin molecules, on the other hand, remained stable in solution and, hence, possessed greater mobility and bridging capacity during and after preparation of the cellophane-starch bonds.

4. Evaluation of strength properties of adhesive films in the Z-direction was much more meaningful in predicting adhesion performance than in the conventional

(in-plane) XY-direction. This was attributed to better correspondence of specimen size and orientation to that present in effective adhesion testing.

5. Stress concentrations were introduced in starch-cellophane bonds by abrasion of the adherend surfaces. However, in the systems of water-cellophane, epoxy-cellophane, epoxy-starch, and metal-epoxy, abrasion was necessary to obtain satisfactory adhesion. The reason for this difference was attributed to the low gap-bridging ability of water, the low availability of the unabraded cellulose surfaces in the absence of starch, and/or the low mobility of the epoxy adhesive.

6. The function of the starch adhesives was to "bridge" or fill in the voids between the two adherends, as evidenced by the fact that the minimum amount of adhesive required to attain maximum adhesion corresponded with the size of the hills and valleys on the adherend surfaces and the void space between them. Increase in the amount of adhesive beyond this amount merely served to decrease strength, probably due to increased stress concentrations in the thicker films.

The cellophane films possessed some surface impurities as evidenced by the small, but significant increase in adhesion produced by solvent cleansing. Diffusion of starch into the cellophane did not overcome this loss in adhesion which indicated that the adsorption theory of adhesion is more significant to this system than the mechanical theory. This was confirmed by the fact that (observable) diffusion was <u>not</u> needed to obtain maximum effective adhesion.

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APPENDIX I

PREPARATION OF PURIFIED AMYLOSE

Figure 26 outlines the sequence of operations used. The details of procedure are as follows: (The paragraph numbers also correspond to the steps in Fig. 26.)

1. Initial dispersion of the whole, methanol-extracted amylose was carried out in a 70-liter stainless steel vessel equipped with indirect steam and oil heating. The charge was as follows:

Water, distilled	43.7
Amylose, dry basis	1000 grams
n-Butanol	6.0 liters
Buffer, pH 6.2 (16.5% KH_2PO_4, 3.6% K_2HPO_4)	160 ml.

The water and buffer were added to the vessel first and preheated to 90°C. to drive out dissolved air. The amylose was screened through a 150-mesh sieve to remove any large aggregates and then dispersed in the butanol. The butanol dispersion of starch was added to the water in the vessel and the vessel was sealed. Nitrogen gas was passed into the solution for 10 minutes to minimize the amount of oxygen in the digester. The steam and heated oil were turned on at maximum rate. After 30 seconds and also at one minute, air was vented from the top of the vessel. The temperature reached 145°C. in eight minutes and 160°C. in 13 minutes, at which point the vessel was emptied in one minute by blowing under pressure.

2. The amylose-butanol-water mixture was placed in a large stainless steel tank in a 95°C. water bath. The solution was diluted back to 50 liters total volume with eight liters water and 2 liters butanol. The pH of the solution was 6.3 indicating that hydrolytic degradation was not severe. The mixture was centrifugated (Sharples Supercentrifuge, 50,000 r.p.m.) while hot to remove any undissolved matter. This residue was 2.9% by weight of the initial amylose.

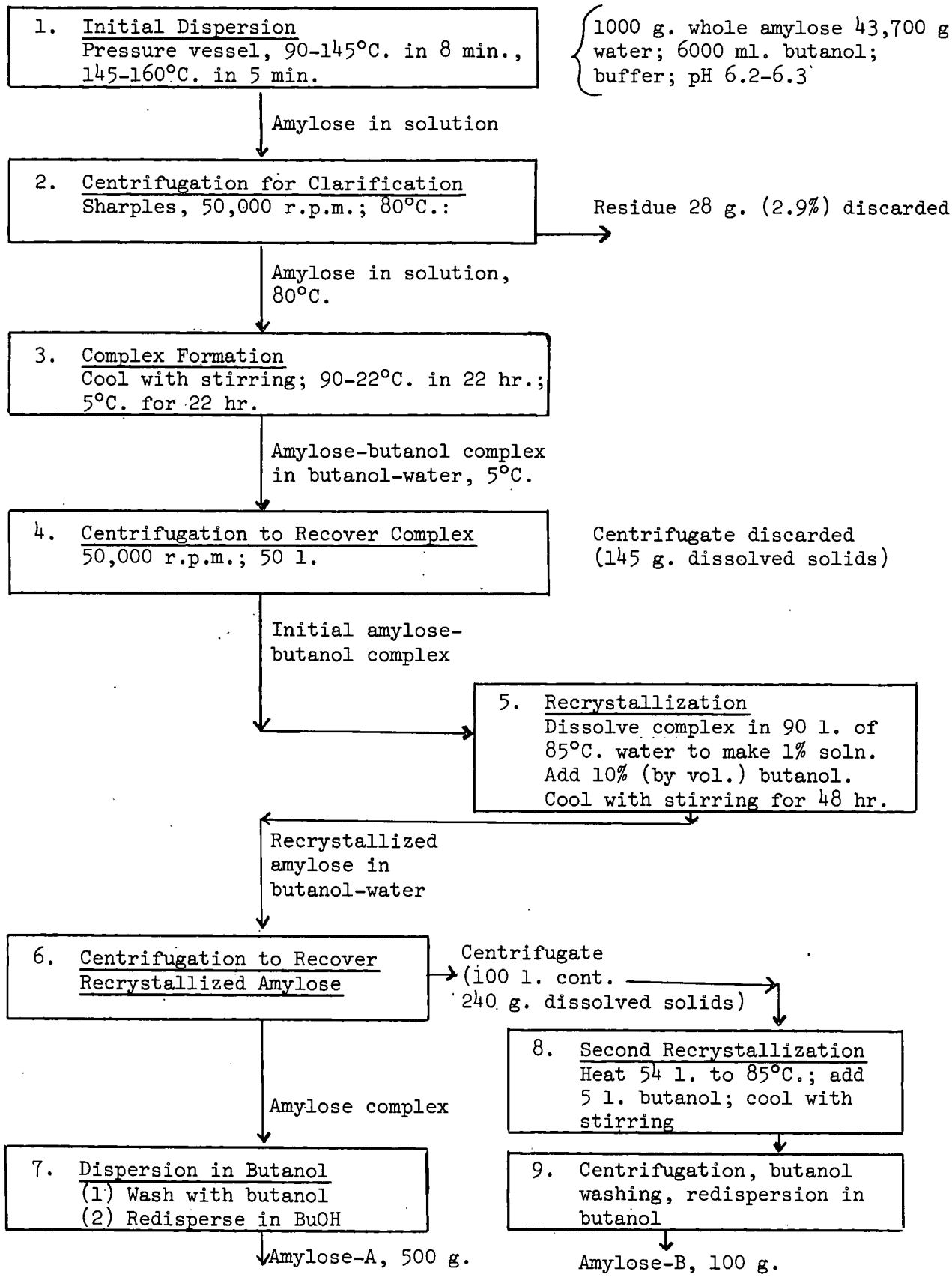


Figure 26. Outline for Large-Scale Preparation of Amylose

3. The hot centrifugate was returned to a stirrer-equipped vessel in the water bath. The solution was allowed to cool slowly, with constant stirring, from 90 to 22°C. over a 22-hour period. The solution was then placed in a cold room (4 to 5°C.) for 22 hours with constant stirring in order to complete the complexing of the amylose with butanol.

4. The initial amylose-butanol complex was recovered by Sharples' centrifugation at 50,000 r.p.m. The isolated complex was stored in butanol to minimize retrogradation of the amylose while the entire 50 liters were centrifugated. The centrifugate containing approximately 145 g. of starch material was discarded.

5. The butanol was poured from the amylose complex and 10 liters of 80°C. water was pasted into the complex. This was done to break down lumps in the complex. The water dispersion of the amylose complex was then diluted with 80 liters of 85°C. water to yield an amylose solution of about 1% concentration. Recrystallization of the amylose was carried out by adding 10% by volume of butanol to the hot solution and slowly cooling with continuous stirring. Centrifugation of 20 liters of the solution prior to cooling yielded no noticeable residue, so further clarification was not undertaken. The solution was cooled slowly from 81 to 29°C. in 17 hours. Then cooling water was passed into the water bath and caused a decrease of solution temperature to 21°C. in two hours. The dispersion was stored two days at 4-5°C.

6. The recrystallized amylose complex was recovered by centrifugation at 35,000 r.p.m. in the Sharples Supercentrifuge. The amylose paste was stored in 1-1/2 liters of butanol during the period required to process the entire 100 liters.

7. The amylose complex was dispersed in the butanol for one minute in a large Waring Blendor and then filtered on a 24-cm. Buchner funnel. The amylose

residue was washed with one liter of butanol, redispersed in the blendor with two liters of fresh butanol, and stirred slowly for 12 hours to allow opportunity for the diffusion of water from the complex. The amylose was recovered by filtration, washed again with butanol, and finally redispersed in 2-1/2 liters of butanol, using the blendor. This butanol dispersion contained 500 grams of amylose and comprised the master stock dispersion called amylose-A. Storage in butanol in the virtual absence of water preserved the water solubility of the amylose.

The centrifugate from the recrystallization of the amylose (Step 6) was found to contain about 240 grams of dissolved material. A trial attempt at recovering a portion of this material proved successful; therefore, slightly over one-half of the centrifugate (54 liters) was processed as follows: Five liters of butanol were added. The solution was heated to 92°C. with stirring and then cooled very slowly with constant stirring to facilitate complexing. Centrifugation served to recover the complex. This resulted in 100 grams (70% recovery of the solids) as an amylose complex (called Amylose-B). This amylose also was stored under butanol as in Step 7.

APPENDIX II

TABLE XXXI

CALIBRATION DATA RELATING FREE IODINE CONCENTRATION TO EMF FOR 100 ML. OF SOLUTION 0.05N KCl AND 0.05N KI

Conditions: Temperature of Solution = 23.3 ± 0.1°C.
Electrodes--bare platinum wire and saturated calomel

Iodine, ml.	Total Iodine Added, mg. x 10^2	Emf,, volts		
		Run 1	Run 2	Run 3
0.00	0.00	--	--	0.1890
0.05	1.14	0.2220	0.2221	--
0.10	2.28	0.2315	0.2314	--
0.20	4.56	0.2403	0.2401	--
0.25	5.00	--	--	0.2428
0.30	6.84	0.2472	0.2472	--
0.40	9.12	0.2510	0.2512	--
0.50	10.00	--	--	0.2528
0.50	11.4	0.2540	0.2541	--
0.75	15.0	--	--	0.2578
0.75	17.1	0.2595	0.2595	--
1.00	20.0	--	--	0.2619
1.00	22.8	0.2635	0.2633	--
1.25	25.0	--	--	0.2650
1.25	27.5	0.2665	0.2666	--
1.50	30.0	--	--	0.2673
1.50	34.2	0.2690	0.2691	--
1.75	35.0	--	--	0.2693
2.00	40.0	--	--	0.2710
2.00	45.6	0.2726	0.2725	--
2.50	50.0	--	--	0.2740
2.50	57.0	0.2756	0.2756	--
3.00	60.0	--	--	0.2762
3.00	68.4	0.2778	0.2777	--
3.55	71.0	--	--	0.2782
4.00	80.0	--	--	0.2801
4.00	91.2	0.2814	0.2815	--
5.05	101.0	--	--	0.2827
5.00	114.0	0.2842	0.2843	--
6.00	136.8	0.2862	0.2860	--

TABLE XXXI (Continued)

CALIBRATION DATA RELATING FREE IODINE CONCENTRATION TO EMF FOR 100 ML. OF SOLUTION 0.05N KCl AND 0.05N KI

Conditions: Temperature of Solution = 23.3 ± 0.1°C.
Electrodes--bare platinum wire and saturated calomel

Iodine, ml.	Total Iodine Added, mg. x 10^2	Emf., volts		
		Run 1	Run 2	Run 3
7.00	159.6	0.2888	0.2881	--
8.00	160.0	--	--	0.2885
8.50	170.0	--	--	0.2893
9.00	180.0	--	--	0.2900
8.00	182.4	0.2903	0.2900	--
9.00	205.2	0.2913	0.2912	--
10.00	228.0	0.2925	0.2923	--

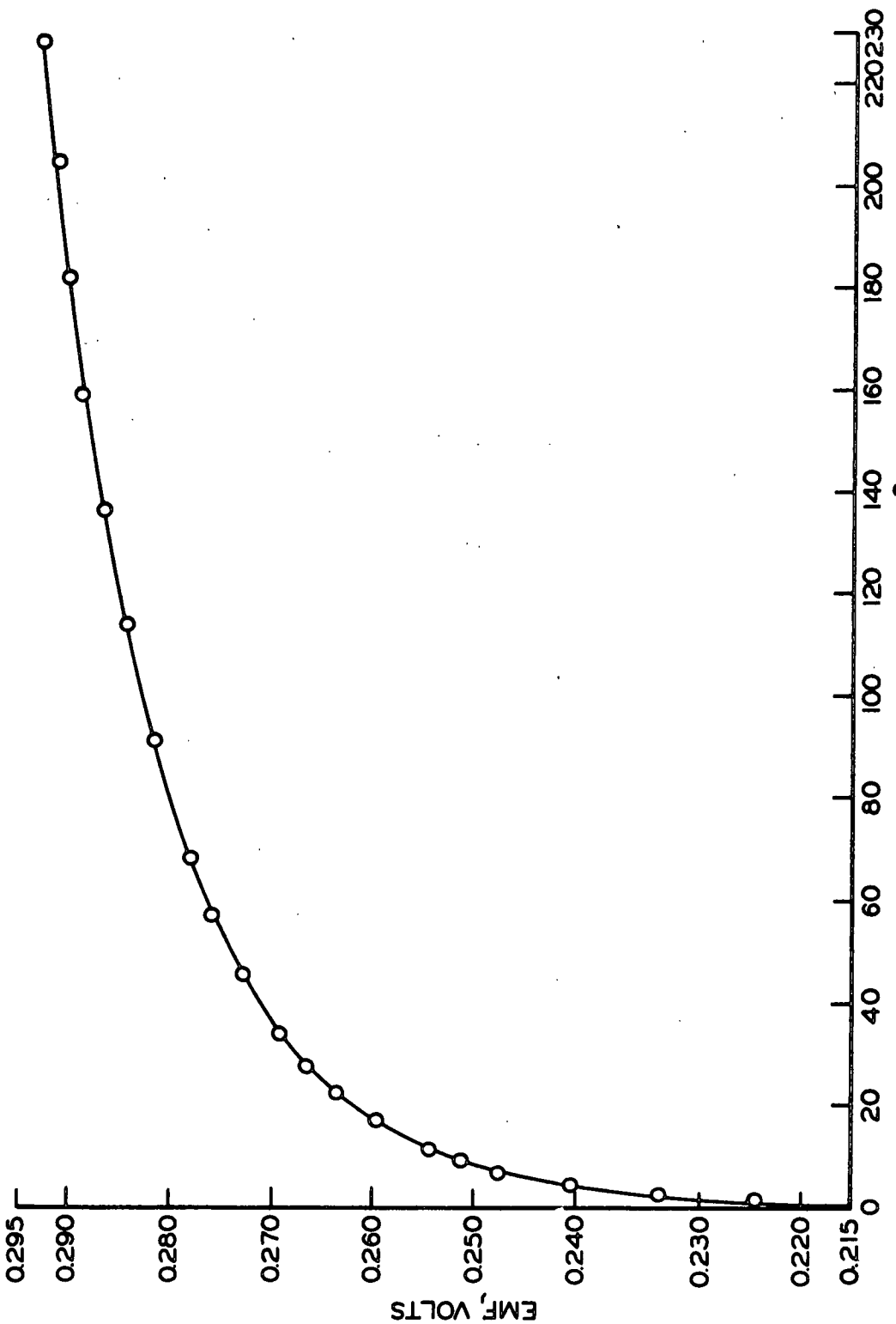


Figure 27. Calibration Curve, Free Iodine vs. EMF

APPENDIX III

TABLE XXXII

IODINE-BINDING VALUE DATA AMYLOSE AND AMYLOPECTIN

Conditions: Temperature of Solution = 23.3 ± 0.1°C.
Electrodes--platinum wire and saturated calomel
Solution--initial volume = 100 ml.
salt concn. = 0.05N KCl, 0.05N KI

Iodine Added, ml.	Total Iodine Added, mg. x 10^2	Emf., volts	Free Iodine from Emf., mg. x 10^2	Bound Iodine, mg. x 10^2
		Amylopectin, 904 mg.		
0.80	16	0.2220	1.1	15
2.10	42	0.2353	2.4	40
3.95	79	0.2405	4.6	74
5.95	119	0.2470	6.8	112
7.10	142	0.2528	10.0	132
7.65	153	0.2549	12.1	141
9.55	191	0.2620	20.0	171
10.70	214	0.2655	26.0	188
13.05	261	0.2700	37.0	224
14.75	295	0.2725	46.0	249
15.85	317	0.2742	51.0	266
18.40	368	0.2764	62.0	306
19.60	392	0.2777	68.0	324
		Amylose-A, 41.28 mg.		
5.0	114	0.2238	1.2	113
10.0	228	0.2255	1.5	226
15.0	342	0.2269	1.8	340
25.0	570	0.2293	2.0	568
30.0	684	0.2330	2.6	681
31.0	707	0.2345	2.9	704
33.0	752	0.2390	4.0	748
34.0	775	0.2435	5.7	769
35.0	798	0.2460	6.6	791
36.0	821	0.2532	10.8	810

TABLE XXXII (Continued)

IODINE-BINDING VALUE DATA AMYLOSE AND AMYLOPECTIN

Conditions: Temperature of Solution = 23.3 ± 0.1°C.
Electrodes--platinum wire and saturated calomel
Solution--initial volume = 100 ml.
salt concn. = 0.05N KCl, 0.05N KI

Iodine Added, ml.	Total Iodine Added, mg. x 10^2	Emf., volts	Free Iodine from Emf., mg. x 10^2	Bound Iodine, mg. x 10^2
		Amylose-A, 41.28 mg. (Cont'd.)		
38.0	866	0.2625	21.5	844
40.0	921	0.2725	46.0	875
44.0	1002	0.2795	77.5	925
45.0	1026	0.2801	81.0	945
46.8	1070	0.2834	105.0	966
49.0	1117	0.2850	123.0	994
		Amylose-A, 40.14 mg.		
5.0	114	0.2245	1.2	113
15.0	342	0.2295	2.0	340
25.0	570	0.2315	2.2	568
30.0	684	0.2355	3.0	681
31.0	707	0.2370	3.5	703
33.0	752	0.2438	5.9	746
35.0	798	0.2548	7.2	791
37.0	844	0.2645	24.5	820
40.0	912	0.2743	52.0	860
42.0	958	0.2792	72.5	885
44.0	1003	0.2818	92.0	911
46.2	1052	0.2845	117.0	935
		Amylose-B, 60.50 mg.		
5.0	114	0.2185	0.9	113
25.0	570	0.2213	1.0	569
35.0	798	0.2255	1.6	796
43.0	980	0.2300	2.0	978
50.0	1140	0.2445	6.0	1134
52.0	1186	0.2540	11.4	1175
55.0	1254	0.2655	26.4	1228
60.0	1368	0.2769	62.8	1305
65.0	1482	0.2830	103.0	1379
69.3	1579	0.2860	136.0	1443

TABLE XXXII (Continued)

IODINE-BINDING VALUE DATA AMYLOSE AND AMYLOPECTIN

Conditions: Temperature of Solution = 23.3 ± 0.1°C.
Electrodes--platinum wire and saturated calomel
Solution--initial volume = 100 ml.
salt concn. = 0.05N KCl, 0.05N KI

Iodine Added, ml.	Total Iodine Added, mg. x 10^2	Emf., volts	Free Iodine from Emf., mg. x 10^2	Bound Iodine, mg. x 10^2
		Amylose-B, 59.07 mg.		
5.0	114	0.2175	0.4	114
15.0	342	0.2204	1.0	341
25.0	570	0.2212	1.0	569
43.0	980	0.2249	1.6	978
50.1	1142	0.2485	8.0	1134
52.0	1186	0.2580	15.6	1170
53.5	1220	0.2640	23.0	1197
55.0	1254	0.2681	32.5	1221
60.0	1368	0.2778	67.0	1301
65.0	1482	0.2834	106.5	1375
69.8	1591	0.2870	143.0	1448

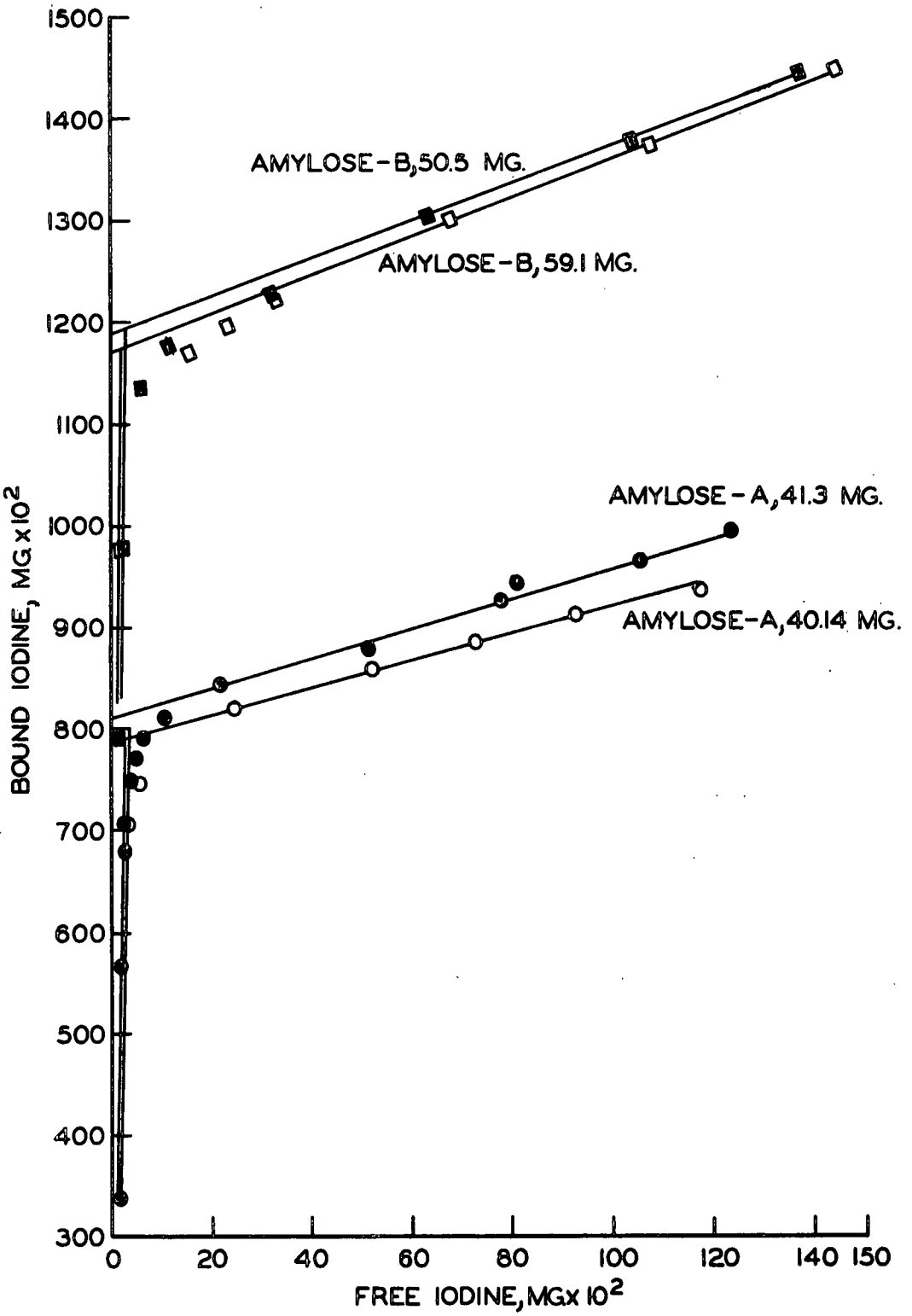


Figure 28. Determination of Iodine Binding Value; Free Iodine vs. Bound Iodine

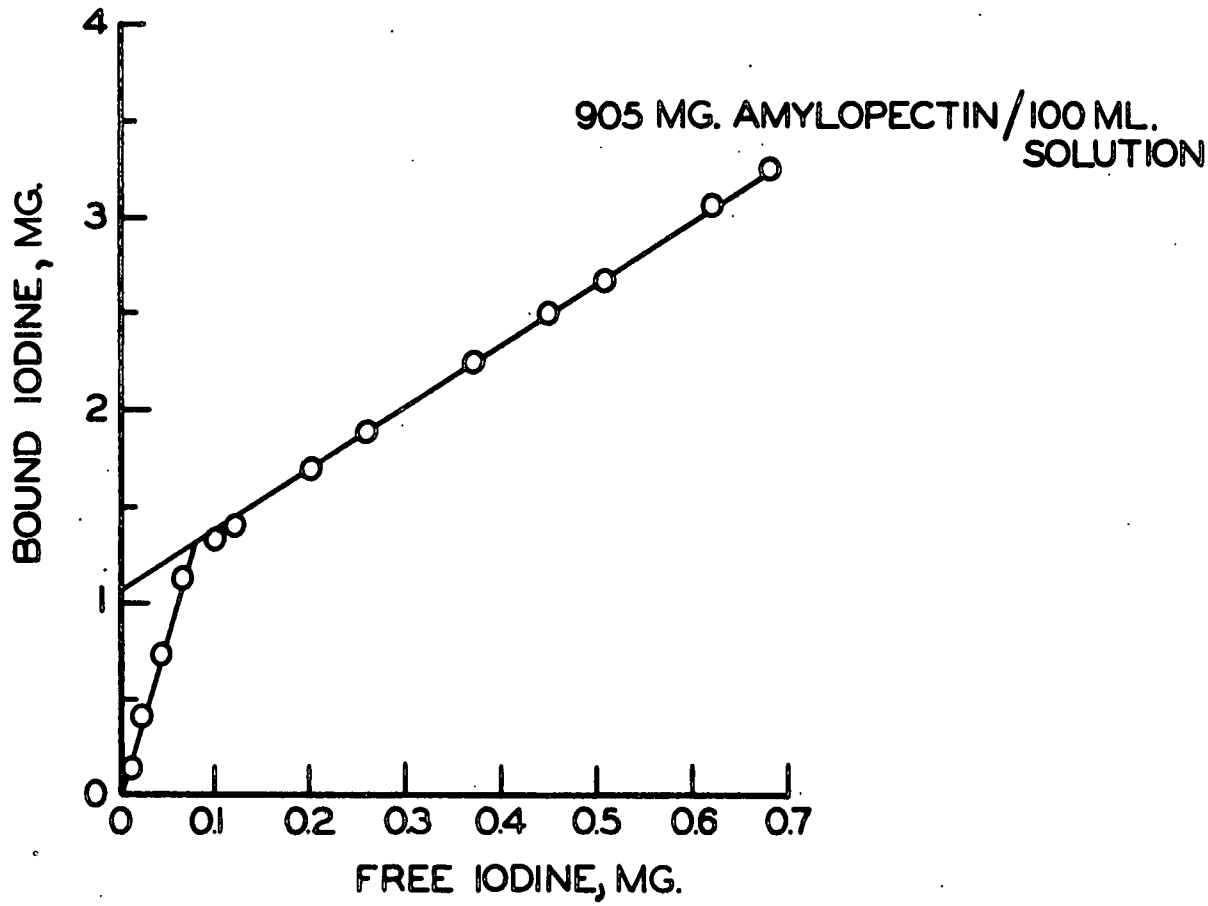


Figure 29. Determination of Iodine Binding Value of Amylopectin

APPENDIX IV

PROCEDURE FOR HYDROLYSIS OF AMYLOSE

1. Dispersed 150 g. (a.d.) of defatted waxy maize starch in 5000 ml. of water by heating and stirring 30 minutes at 99°C.

2. Dispersion was centrifuged in a Sharples supercentrifuge at 50,000 r.p.m. at a rate of 20 ml./min.

3. The centrifuged solution (4270 ml.) was placed in a 5-liter, 3-necked, round-bottomed flask equipped with a condenser, magnetic stirrer, thermometer, and a helium gas inlet tube; 43.60 g. of potassium acid phthalate (0.05M) were added to buffer to a pH of 4.24 at 100°C.

4. Dispersion was maintained at 100°C. by refluxing. Stirring and addition of helium were carried out continuously during the course of the run.

5. Samples of 700 ml. were removed by vacuum aspiration at the following time intervals: 1, 3, 10, 30.5, 70, and 141 hr.

6. Each fraction was immediately precipitated by slowly pouring it into 1500 ml. of rapidly agitated 95% ethanol.

7. The precipitates were washed with 80% ethanol and redissolved in hot water. A pH check showed that all of the buffer was not removed, so one to three additional precipitations were made to purify the amylopectin. When an amylopectin solution of pH 6.2 or greater was obtained, it was recovered by freeze drying in an NRC dehydration unit.

8. The recovery of amylopectin ranged from 91 to 98% for the various fractions.

APPENDIX V

TABLE XXXIII

DETERMINATION OF REFRACTIVE INDEX GRADIENT OF AMYLOSE IN WATER[a]

Sample	Concentration, g./ml. x 10^2	Drum Reading, $\underline{D}$	$(\underline{D} - \underline{D}_o)$		$\underline{dn}/\underline{dc}$, cc./g.
Amylose-B	0.673	914	888		0.153
Amylose-A	0.411	555	529		0.150
Amylose-A	0.245	357	331		0.157
				Mean	0.153

[a] Rayleigh Interferometer was used with this equation:

$\underline{dn}/\underline{dc} = (\underline{D} - \underline{D}_o)\lambda/47\ \underline{c}\ \underline{l}$

$\underline{dn}/\underline{dc}$ = specific refractive index gradient, cc.g.,

$\underline{D}$ = instrument drum reading for the solution, arbitrary units,

$\underline{D}_o$ = instrument drum reading for the solvent, arbitrary units, 26 for water

λ = wavelength of light, 5.461×10^{-5} cm.

$\underline{c}$ = concentration of polymer solution, g./ml.

$\underline{l}$ = path length, 1.00 cm.

APPENDIX VI

LIGHT SCATTERING MOLECULAR WEIGHT CALCULATIONS

For the amylose-water system and using light of 4358 A. wavelength, Equation (17) ($\underline{H} = 32\,\pi^3 \underline{n_o}^2\,(\underline{dn/dc})^2/3\lambda^4\underline{N}$) becomes equal to 6.30×10^{-6}. For Brice-Phoenix Photometer No. 1937, the absolute turbidity due to solute, $\tau\theta$, is determined from the equation

$$\tau\theta = \phi(FG_\theta/G_o - FG_\theta/G_o)\,(\sin\theta)/(1 + \cos^2\theta) \qquad (15)$$

where

$\tau\theta$ = solute turbidity at angle θ, $cm.^{-1}$,

ϕ = constant dependent on instrument geometry, solvent, and wavelength of light used,

$\underline{F}$ = filter transmittance factor,

$\underline{G_\theta/G_o}$ = ratio of galvanometer deflection at angle θ to that at 0° for the solution,

$\underline{G_\theta'/G_o'}$ = ratio of galvanometer deflection at angle θ to that at 0° for the solvent, and

$\sin\theta$ = factor to compensate for change in solution volume viewed with change in viewing angle, and

$1/(1 + \cos^2\theta)$ = correction for the use of unpolarized light

When scattering ratios are determined only at 90°, Equation (15) reduces to

$$\tau_{90°} = \phi\,(FG_{90}/G_0 - FG'_{90}/G_0) \qquad (16)$$

where

$$\phi = [16TD/3(1.045)h][n_o^2\,R_W/R_c]\,(a)(r/r'), \qquad (17)$$

where

$\underline{TD}$ = diffuse transmittance of reference opal glass times diffusor correction factor, 0.267,

1.045 = correction for reflection of primary beams at emergent face of the cell.

$\underline{h}$ = diaphragm width; 1.20 cm.,

n_o = refractive index of solvent; 1.337

R_W/R_c = correction for refractive effects; 1.066,

a = working standard constant; 0.0397, and

r/r' = correction factor employed when narrow diaphragm (0.4 cm.) is used instead of the standard diaphragm; $r/r' = 1.232$.

Substitution of the constants of Equation (17) into Equation (15) gives the following simplified expressions for absolute turbidity of amylose solutions at 90°:

$$\tau_{90°} = 0.0864\ (FG_{90}/G_0 - FG'_{90}/G'_0) \text{ for standard diaphragm} \qquad (18)$$

and

$$\tau_{90°} = 0.1065\ (FG_{90}/G_0 - FG'_{90}/G_0) \text{ for narrow diaphragm} \qquad (19)$$

Thus, using H equal to 6.30×10^{-6} and $\tau_{90°}$ calculated from (18) or (19) above, the $(Hc/\tau)_{90°}$ ratio was obtained for a series of concentrations. By plotting (Hc/τ_{90}) vs. c and extrapolating to $c=0$, the value of (Hc/τ) $c = 0$, $\theta = 90°$ was obtained. The molecular weight was calculated as the reciprocal of $(Hc/\tau)_{\substack{c = 0 \\ \theta = 90°}}$. This was corrected for dissymmetry by use of the $P(\theta)$ factor [determined from intrinsic dissymmetry measurements and tables (133, 134)] to yield the corrected weight average molecular weight, $\overline{M}_w$.

Fluorescence and depolarization corrections were not made because initial checks showed them to be small.

The calculations for amylopectin were identical to the above except that a different dn/dc value was used in the equation for H.

APPENDIX VII

TABLE XXXIV

CALIBRATION DATA: AMYLOSE CONCENTRATION VS. ABSORBANCE

(Wavelength: 625 nm.; iodine: 10 mg./100 ml.; KI: 15 mg./100 ml.)

Solution	Amylose Concentration, mg./l.	Absorbance, A.
Aqueous, neutral	1.01	0.033
	2.02	0.068
	3.03	0.102
	4.04	0.139
	5.05	0.173
	5.30	0.182
	7.07	0.243
	8.45	0.280
	10.1	0.349
	10.6	0.363
	15.15	0.518
	15.90	0.553
	20.2	0.701
	21.2	0.731
	30.3	1.06
	35.35	1.22
Aged aqueous, neutral (aged 6 days)	5.05	0.168
	10.1	0.339
	15.15	0.512
	20.2	0.691
	25.25	0.870
Aqueous, acidic (50 ml. of 1:10 concd. HCl:H_2O per 100 ml. solution)	1.69	0.054
	3.38	0.107
	5.07	0.155
	6.76	0.208
	8.45	0.252
	11.82	0.317
	16.9	0.445
	25.4	0.610
	33.8	0.796

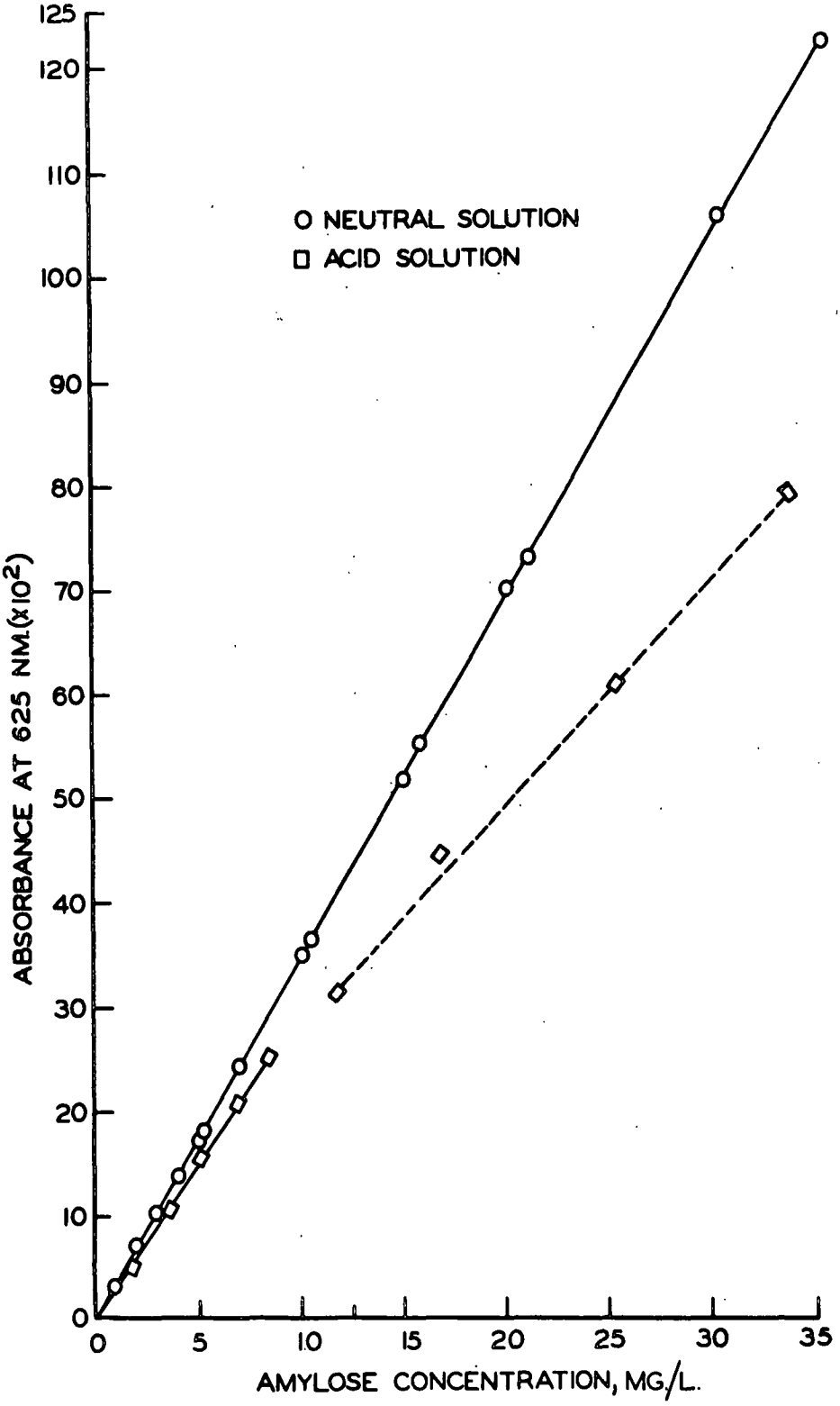


Figure 30. Calibration Curves: Amylose Concentration vs. Absorbance

TABLE XXXV

CALIBRATION DATA FOR AMOUNT OF AMYLOSE BETWEEN TWO PUD-O CELLOPHANE FILMS VS. ABSORBANCE

Assembly	Absorbance at 625 nm. Specimen 1	Specimen 2	Specimen 3	Specimen 4	Specimen 5	Absorbance, mean	Amylose, g./m.^{2}	90% Confidence Range of Absorbance Mean	Coefficient of Variation, %
B	0.021	0.015	0.023	0.020	0.018	0.020	0.028	±0.0014	13.0
	0.022	0.022	0.020	0.018	0.021				
C	0.048	0.040	0.046	0.038	0.043	0.043	0.048	±0.0017	7.5
	0.042	0.043	0.042	0.046	0.041				
D	0.071	0.083	0.088	0.078	0.078	0.082	0.104	±0.0036	8.3
	0.084	0.082	0.092	0.081	0.080				
E	0.160	0.172	0.169	0.165	0.182	0.170	0.207	±0.0037	4.2
	0.168	0.168	0.175	0.172	0.169				
A	0.172	0.178	0.163	0.180	0.172	0.176	0.230	±0.0044	4.8
	0.176	0.170	0.173	0.182	0.189				
F	0.382	0.351	0.350	0.395	0.366	0.370	0.430	±0.0093	4.8
	0.375	0.350	0.370	0.395	0.367				
G	0.552	0.587	0.539	0.585	0.611	0.573	0.690	±0.0122	4.1
	0.564	0.562	0.547	0.598	0.592				

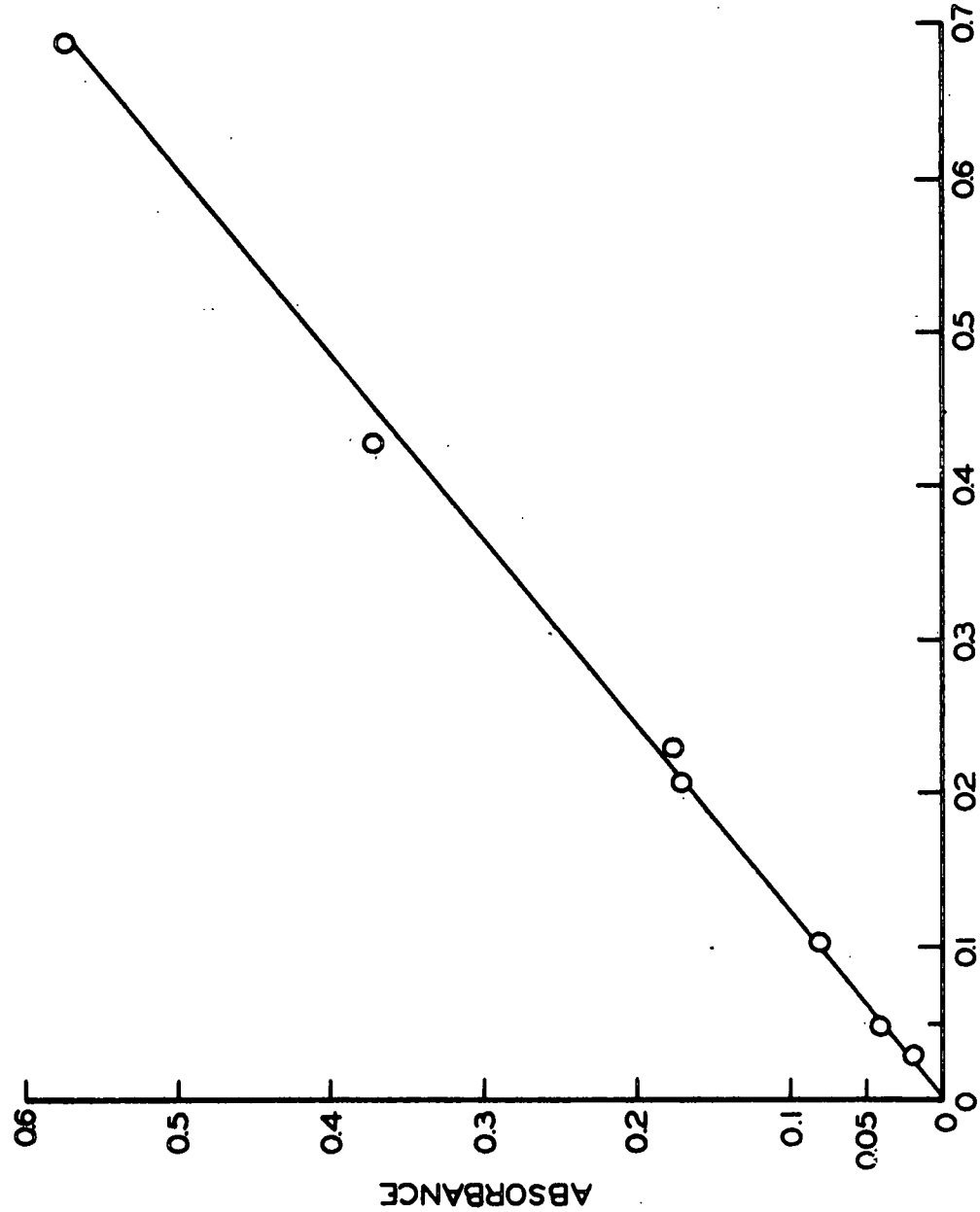


Figure 31. Amylose Content Between Cellophane Films vs. Absorbance at 625 nm.

APPENDIX IX

TABLE XXXVI

LIGHT-SCATTERING DATA FOR AMYLOPECTIN AND AMYLOSE

Starch Code	Concentration, g./ml. x 10^3	$(Hc/\tau)_{\theta=90°}$	Intrinsic Disymmetry, [Z]	Particle Scattering Factor, 1/P(90°)
AMP-121	1.280	0.480 x 10^{-6}		
Whole	3.621	0.522		
Amylopectin	5.414	0.544		
	7.243	0.821		
	8.804	0.720	1.86	1.52
DF-5-EX	0.801	2.383 x 10^{-6}		
Amylopectin	2.121	2.668		
	3.518	2.941		
	5.800	3.180		
	8.082	3.679	1.27	1.17
DF-6-SII	0.960	4.402		
Amylopectin	2.802	4.402		
	4.196	4.861		
	6.011	4.941		
	8.043	5.322	1.12	1.08
DF-5-L	1.283	4.611 x 10^{-6}		
Amylopectin	2.269	4.702		
	3.764	5.083		
	5.703	5.590		
	7.721	6.162	1.04	1.028
DF-6	1.441	5.880 x 10^{-6}		
Amylopectin	3.278	6.363		
	4.939	6.504		
	7.633	7.121		
	9.804	7.381	1.03	1.022
DF-6-SIII	1.082	0.801 x 10^{-5}		
Amylopectin	3.248	0.722		
	5.998	0.925		
	7.599	1.163		
	9.110	1.210	1.0	1.00

TABLE XXXVI (Continued)

LIGHT-SCATTERING DATA FOR AMYLOPECTIN AND AMYLOSE

Starch Code	Concentration, g./ml. x 10^3	$(Hc/\tau)_{\theta=90°}$	Intrinsic Disymmetry, [Z]	Particle Scattering Factor, $1/P(90°)$
DF-5-VL Amylopectin	2.003	2.521×10^{-5}		
	5.211	2.842		
	6.472	2.98		
	7.624	2.721		
	9.613	2.725	1.00	1.00
DF-5-IH Amylopectin	0.811	5.761×10^{-5}		
	2.802	5.832		
	4.540	6.183		
	6.063	6.138		
	8.680	5.963	1.00	1.00
A-144 Whole Amylose	0.191	1.80×10^{-6}		
	0.474	1.77		
	0.790	1.77		
	1.111	1.78		
	1.580	1.73	2.10	2.01
Hydrolyzed 0.5-Hr. Amylose	0.222	3.21×10^{-6}		
	0.449	3.30		
	0.701	3.21		
	0.913	3.21		
	1.350	3.20	1.52	1.39
Hydrolyzed 1.0-Hr. Amylose	0.219	4.62×10^{-6}		
	0.701	4.60		
	0.912	4.61		
	1.048	4.63		
	1.390	4.61	1.34	1.26
Hydrolyzed 3.0-Hr. Amylose	0.221	1.45×10^{-5}		
	0.549	1.41		
	0.779	1.42		
	1.050	1.38		
	1.465	1.40	--	1.00

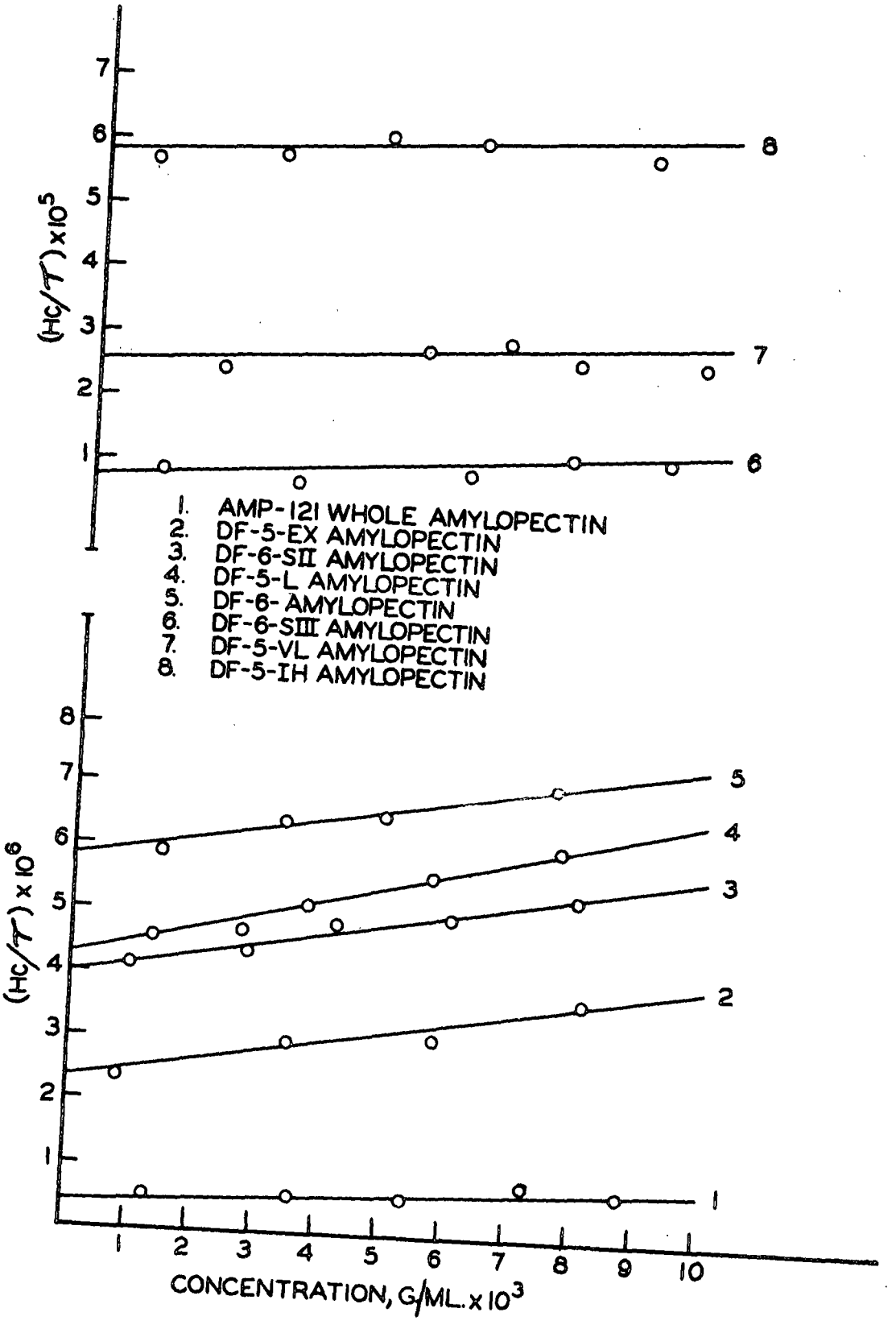


Figure 32. Amylopectin Light Scattering Turbidity vs. Concentration Plots

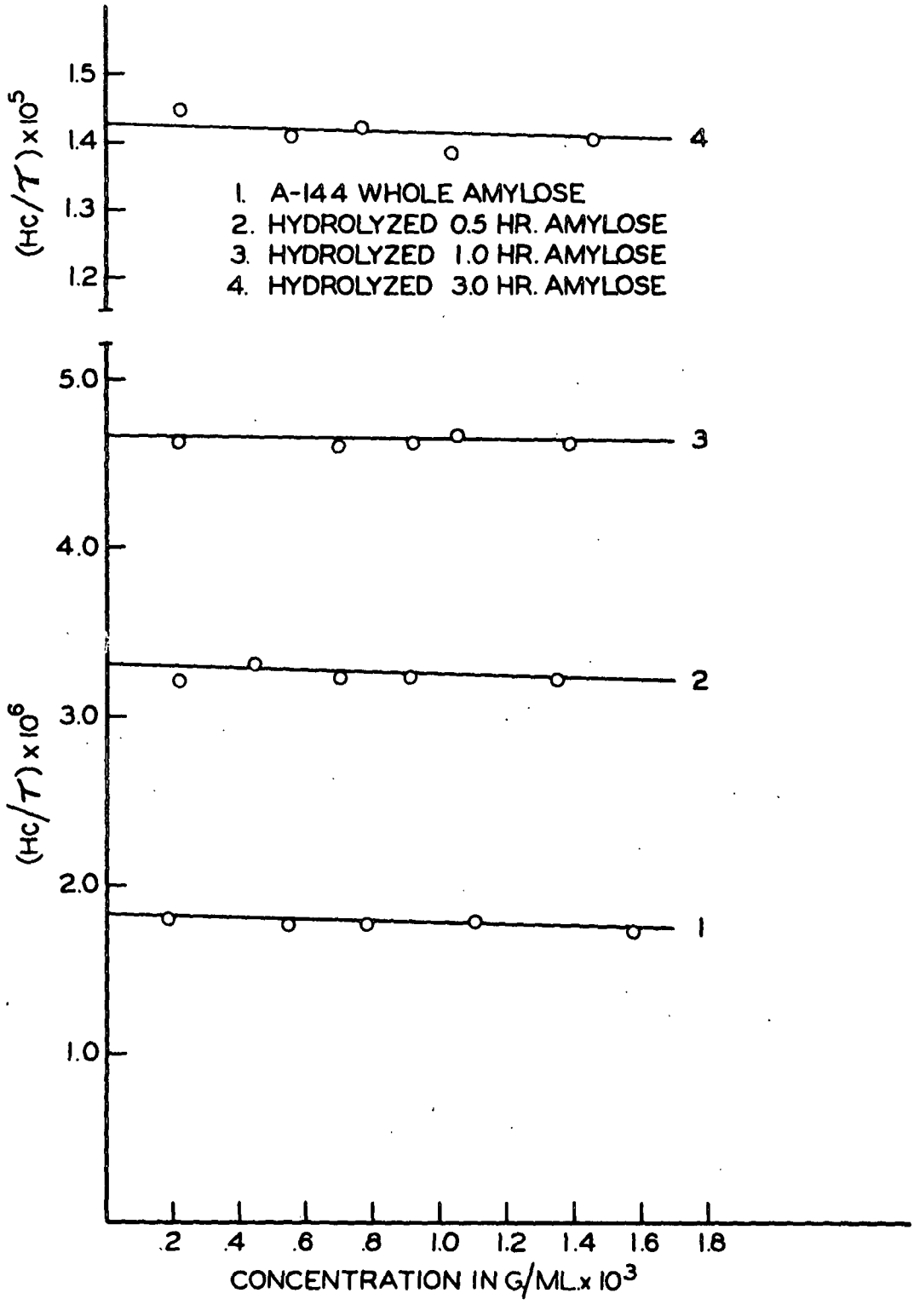


Figure 33. Amylose Light-Scattering Turbidity vs. Concentration Plots

TABLE XXXVII

VISCOSITY DATA AND SUMMARY OF CALCULATIONS FOR AMYLOSE SOLUTIONS

Solution	Concentration, g./100 ml.	Efflux Time, solvent, sec.	Efflux Time, solution, sec.	Specific[a] Viscosity, η_{sp}	Viscosity No., η_{sp}/c	Limiting[b] Viscosity No., $[\eta]$
A-42	0.176	155.9	169.1	0.0845	0.481	
in water	0.126	155.9	165.2	0.0575	0.474	
	0.080	155.9	161.65	0.0368	0.459	
	0.055	155.9	159.85	0.0252	0.458	
	0.028	155.9	158.10	0.0140	0.492	0.47
B-31	0.149	158.5	175.7	0.1085	0.730	
in water	0.118	158.5	171.65	0.0830	0.703	
	0.074	158.5	165.2	0.0423	0.572	
	0.052	158.5	161.8	0.0208	0.400	0.61
A-47	0.533	155.3	202.35	0.3033	0.569	
in water	0.381	155.3	187.85	0.2099	0.551	
	0.296	155.3	180.2	0.1606	0.542	0.51
A-47	0.205	161.8	195.8	0.2097	1.023	
in 0.61N KOH	0.133	161.8	184.0	0.1369	1.028	
	0.089	161.8	178.0	0.1001	1.127	
	0.053	161.8	171.6	0.0603	1.132	1.13
B-47 in	0.482	161.8	344.9	1.131	2.347	
0.61N KOH	0.313	161.8	270.9	0.674	2.151	
	0.209	161.8	231.0	0.427	2.046	
	0.125	161.8	201.8	0.247	1.971	1.83

[a] η_{sp} = (efflux time solution/efflux time solvent) - 1.

[b] $[\eta]$ = limiting viscosity number = "intrinsic viscosity" = $\lim_{c \to o} \eta_{sp}/c$; Units: dl/g.

APPENDIX XI

TABLE XXXVIII

AGING OF AMYLOSE SOLUTIONS MEASURED BY LIGHT SCATTERING

Amylose Sample	Concn., g./ml. x 10^3	$(1/P(\theta))/(Hc/\tau)$ x $10^6/M_w$ x 10^{-6} (apparent)[a] Hours Aging 9	12.5	24.5	36	50	73	104
A-1	1.58	2.16	2.23	3.14	2.82	--	--	--
		1.77	1.60	1.41	1.24	8.74	0.182	--
		1.22	1.39	2.23	2.29	--	--	--
A-2	1.11	--	2.07	2.06	2.11	2.69	6.13	--
		--	1.64	1.78	1.80	1.56	0.78	0.15
		--	1.26	1.16	1.16	1.72	7.83	--
A-3	0.780	--	2.13	2.07	2.06	2.82	6.13	40.5
		--	1.62	1.72	1.84	1.72	1.44	0.58
		--	1.31	1.20	1.12	1.64	4.25	7.02
A-4	0.474	--	2.13	2.03	2.07	2.30	2.82	--
		--	1.68	1.72	1.88	1.92	2.09	1.32
		--	1.27	1.18	1.10	1.20	1.35	--
B-1	0.994	1.55	1.59	1.56	1.55	1.73	2.06	3.29
		1.17	1.03	1.01	1.07	1.07	1.23	0.021
		1.32	1.55	1.55	1.44	1.62	1.66	122.0
B-2	0.695	--	1.59	1.54	1.54	1.54	2.69	--
		--	1.03	1.13	1.31	1.61	1.73	0.97
		--	1.54	1.37	1.17	0.97	1.56	--
B-3	0.497	--	1.52	1.51	1.49	1.77	3.88	--
		--	1.06	1.18	1.40	1.64	1.69	0.99
		--	1.45	1.28	1.07	1.08	2.30	--
B-4	0.298	--	1.62	1.58	1.56	1.89	--	--
		--	1.03	1.09	1.66	2.03	--	--
		--	1.57	1.45	0.94	0.93	--	--

[a] The three values under each hour and at each amylose concentration are from top to bottom: $1/P(90°)$, Hc/τ x 10^6, M_w x 10^{-6} (apparent).

APPENDIX XII

TABLE XXXIX

DATA ON DETERMINATION OF AMOUNT OF DIFFUSION OF AMYLOPECTIN INTO CELLOPHANE

	Code of Amylopectin-Cellophane Bond Assembly				
	DF-5-EX-G	DF-5-EX-G	DF-5-EX-G	S-II-D	S-II-D
1. Specimen area, $cm.^2$	40.99	45.32	35.18	8.457	8.093
2. Specimen weight, g.	0.3417	0.3779	0.2942	0.0722	0.0693
3. Total specimen, $g./m.^2$	83.41	83.39	83.64	85.38	85.68
4. Total amylopectin, $g./m.^{2a}$	7.41	7.39	7.20	9.38	9.68
5. Weight of both surface washed films, g.	0.3118	0.3453	0.2682	0.0662	0.0631
6. Weight of bond amylopectin, (2-5), g.	0.0301	0.0326	0.0260	0.0060	0.0062
7. Bond amylopectin (6/1) x 10^4, $g./m.^2$	7.34	7.20	7.39	7.12	7.72
8. Bond amylopectin, (7/4) x 100, %	99.0	97.4	96.7	75.9	79.8
9. Diffused amylopectin, %	1.0	2.6	3.3	24.1	20.2
10. Wt. films after hot water extraction, g.	--	--	--	0.0643	0.0618
11. Extracted films, $g./m.^2$	--	--	--	76.03	76.36
12. Extracted films corrected, $g./m.^{2b}$	--	--	--	77.25	77.58
13. Diffused amylopectin <u>not</u> removed during extraction, $g./m.^2$ (12-76.0 $g./m.^2$)	--	--	--	1.25	1.58
14. Diffused amylopectin not extracted, %	--	--	--	55	81

[a] Based on blank = 76.0 $g./m.^2$

[b] Corrected for amount of blank cellophane dissolved during hot water extraction (factor = 1.016).

TABLE XXXIX (Continued)

DATA ON DETERMINATION OF AMOUNT OF DIFFUSION OF AMYLOPECTIN INTO CELLOPHANE

	Bond Assembly Code			
	S-III-D	S-III-D	S-III-D	S-III-D
1. Specimen area, cm.^{2}	8.945	8.594	8.907	8.413
2. Specimen weight, g.	0.0730	0.0703	0.0729	0.0689
3. Total specimen, g./m.^{2}	81.62	81.78	81.84	81.85
4. Total amylopectin, g./m.^{2a}	5.62	5.78	5.84	5.85
5. Weight of both surface-washed films, g.	0.0708	0.0683	0.0707	0.0670
6. Weight of bond amylopectin, (2-5), g.	0.0022	0.0020	0.0022	0.0019
7. Bond amylopectin (6/1) x 10^4, g./m.^{2}	2.48	2.27	2.44	2.22
8. Bond amylopectin, (7/4) x 100, %	44.1	39.2	41.8	37.9
9. Diffused amylopectin, %	55.9	60.8	58.2	62.1
10. Wt. films after hot water extraction, g.	0.0666	0.0644	0.0665	0.0628
11. Extracted films, g./m.^{2}	74.44	74.90	74.63	74.65
12. Extracted films corrected, g./m.^{2b}	75.63	76.10	75.82	75.84
13. Diffused amylopectin <u>not</u> removed during extraction, g./m.^{2} (12-76.0 g./m.^{2})	0	0.10	0	0
14. Diffused amylopectin not extracted, %	0	0	0	0

[a] Based on blank = 76.0 g./m.^{2}.
[b] Corrected for amount of blank cellophane dissolved during hot water extraction (factor = 1.016).

TABLE XXXIX (Continued)

DATA ON DETERMINATION OF AMOUNT OF DIFFUSION OF AMYLOPECTIN INTO CELLOPHANE

	Bond Assembly Code			
	DF-6-E	DF-6-E	DF-6-E	DF-6-E
1. Specimen area, cm.^{2}	8.603	8.348	8.336	8.038
2. Specimen weight, g.	0.9763	0.0741	0.0738	0.0710
3. Total specimen, g./m.^{2}	88.74	88.72	88.58	88.36
4. Total amylopectin g./m.^{2}[a]	12.74	12.72	12.58	12.36
5. Weight of both surface-washed films, g.	0.0701	0.0677	0.0674	0.0652
6. Wt. of bond amylopectin, (2-5), g.	0.0062	0.0064	0.0064	0.0058
7. Bond amylopectin (6/1) x 10^4, g./m.^{2}	7.21	7.62	7.65	7.17
8. Bond amylopectin (7/4) x 100, %	56.6	59.9	60.8	58.0
9. Diffused amylopectin, %	43.4	40.1	39.2	42.0
10. Wt. films after hot water extraction, g.	0.0663	0.0647	0.0642	0.0620
11. Extracted films, g./m.^{2}	77.05	77.52	77.03	77.17
12. Extracted films corrected, g./m.^{2}[b]	78.29	78.76	78.26	78.40
13. Diffused amylopectin not removed during extraction, g./m.^{2} (12-76.0 g./m.^{2})	2.29	2.76	2.26	2.40
14. Diffused amylopectin not extracted, %	41	54.1	45.8	46.2

[a] Based on blank = 76.0 g./m.^{2}.

[b] Corrected for amount of blank cellophane dissolved during hot water extraction (factor = 1.016).

TABLE XXXIX (Continued)

DATA ON DETERMINATION OF AMOUNT OF DIFFUSION OF AMYLOPECTIN INTO CELLOPHANE

	Bond Assembly Code		
	DF-5L-G	DF-5L-G ,	DF-5L-G
1. Specimen area, $cm.^2$	26.58	27.99	35.41
2. Specimen weight, g.	0.2221	0.2334	0.2966
3. Total specimen, $g./m.^2$	83.55	83.40	83.77
4. Total amylopectin, $g./m.^{2a}$	7.55	7.40	7.77
5. Weight of both surface-washed films, g.	0.2086	0.2214	0.2789
6. Wt. of bond amylopectin, (2-5), g.	0.0135	0.0120	0.0177
7. Bond amylopectin (6/1) x 10^4, $g./m.^2$	5.10	4.28	5.00
8. Bond amylopectin (7/4) x 100, %	67.5	57.8	63.1
9. Diffused amylopectin, %	32.5	42.2	36.9

[a]Based on blank = 76.0 $g./m.^2$.
[b]Corrected for amount of blank cellophane dissolved during hot water extraction (factor = 1.016).

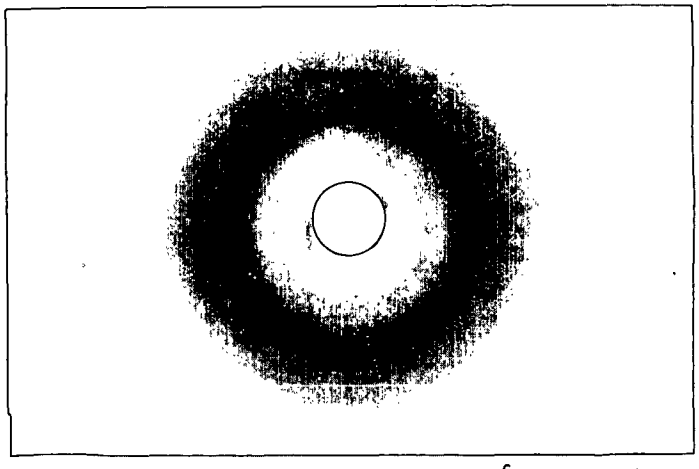
TABLE XXXIX (Continued)

DATA ON DETERMINATION OF AMOUNT OF DIFFUSION OF AMYLOPECTIN INTO CELLOPHANE

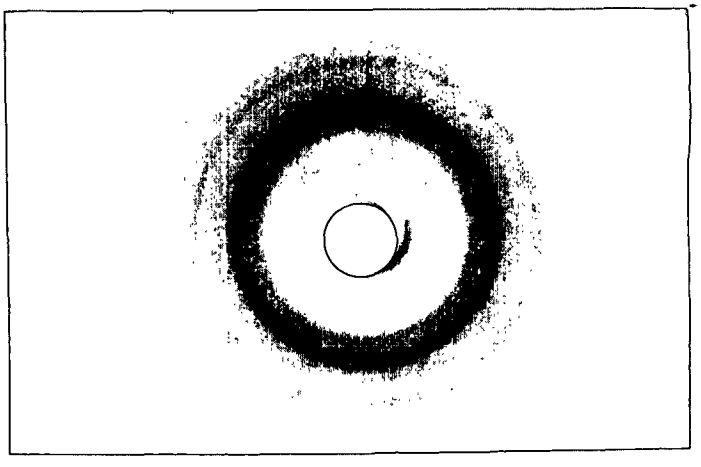
	Bond Assembly Code					
	DF-5-VL-F	DF-5-VL-F	DF-5-VL-F	DF-5-IH E	DF-5-IH E	DF-5-IH E
1. Specimen area, $cm.^2$	22.18	28.30	27.56	35.15	34.89	33.77
2. Specimen weight, g.	0.1845	0.2360	0.2304	0.2929	0.2899	0.2820
3. Total specimen, $g./m.^2$	83.20	83.38	83.82	83.34	82.98	83.52
4. Total amylopectin, $g./m.^{2a}$	7.20	7.38	7.62	7.34	6.98	7.52
5. Weight of both surface washed films, g.	0.1781	0.2286	0.2261	0.2903	0.2820	0.2778
6. Weight of bond amylopectin, (2-5), g.	0.0064	0.0074	0.0043	0.0026	0.0075	0.0042
7. Bond amylopectin (6/1) x 10^4, $g./m.^2$	2.90	2.62	1.57	0.76	2.15	1.25
8. Bond amylopectin (7/4) x 100, %	40.3	36.5	20.5	10.2	30.8	16.7
9. Diffused amylopectin, %	59.7	64.5	79.5	89.8	69.2	83.3

[a] Based on blank = 76.0 $g./m.^2$.
[b] Corrected for amount of blank cellophane dissolved during hot water extraction (factor = 1.016).

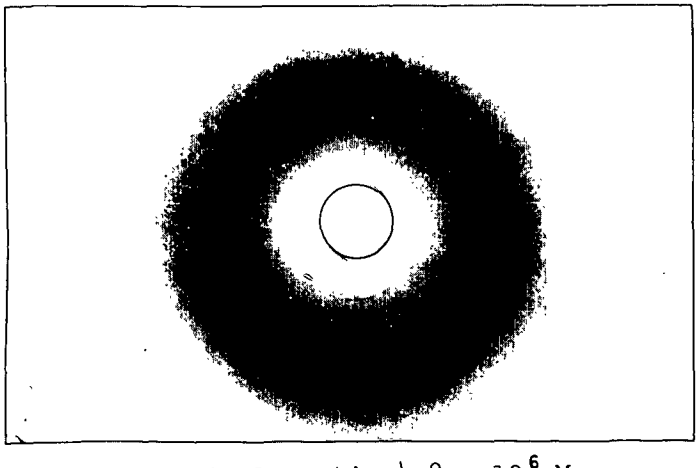
APPENDIX XIII



Whole Amylose, 1.1 x 10^6 $\underline{M}_w$



3.0-Hour Hydrolyzed Amylose 70,000 $\underline{M}_w$



Whole Amylopectin 4.8 x 10^6 $\underline{M}_w$

Figure 31. X-ray Diffraction Patterns of Amylose and Amylopectin Films